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Final Report

CONTAMINATION OF DIESEL ENGINE LUBRICATION OIL BY PLANT OIL DERIVATIVE FUELS

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FINAL REPORT

CONTAMINATION OF DIESEL ENGINE LUBRICATION
OIL BY PLANT OIL DERIVATIVE FUELS
RAE-84-1040

DANIEL L. SHAFER

DEPARTMENT OF CHEMICAL ENGINEERING
MONTANA STATE UNIVERSITY
BOZEMAN, MONTANA 59717
(406) 994-5922

This project involves a laboratory simulation study of the problem of lubrication oil thickening when sunflower oil is used as fuel in extended operation of a diesel engine. Mill grade sunflower oil produced in Montana was the renewable energy source.

Total Project Cost	\$87,548*
DNRC Grant	\$39,548

* The project was also supported by a concurrent grant of \$48,000 from the National Science Foundation.

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ABSTRACT

A research program was conducted to investigate the problems that result when lubricating oil in diesel engines is contaminated by fuel made from vegetable oil. Thermal and oxidative conditions typical for a diesel engine lubrication system were simulated in laboratory equipment. Viscosity rise, production of insoluble gels and loss of alkalinity in the oil were measured.

System variables affecting lube oil degradation were identified and their impacts measured. Oil from several types of Montana plants that might be grown for fuel were evaluated and all of them were found to present the same problem when they contaminate lube oil.

A free radical mechanism was confirmed for the polymerization thickening of sunflower oil triglycerides at conditions of this study. Dissolved copper species strongly catalyzed this polymerization at very low copper concentrations. No other common engine wear metals exhibited any catalytic behavior of significance. The overall mechanism study was complicated by the presence of unknown chemical additives in commercial lubrication oil, but hydrocarbon base stocks without additives could not be extensively used due to rapid generation of insoluble gel.

Progress was made in identifying chemical antioxidants and copper catalyst deactivators and in assessing their efficacy. Continued research will focus on these facets of the problem with safflower oil fuel and diesel locomotive lube oils.

INTRODUCTION

In recent years the escalating price of diesel fuel and the uncertainty of its availability have accelerated research efforts to develop acceptable alternate fuelstocks. Identification of emergency fuel supplies for direct injection diesel engines, widely used in heavy transportation and agriculture, is an area of interest for many researchers (1). Fuel production from renewable biomass, especially oil-bearing plants, is a key area of research. Plant oils or plant oil derivatives obtained with minimal processing may ultimately prove acceptable as fuels for diesel engines, but several technical problems must be overcome.

In Montana a strategy has been devised to make use of plant oil diesel fuels as extenders or substitutes in times of emergency fuel shortage. The Montana strategy identified some research needed to improve the price of safflower oil to \$1.47 per refined gallon if the 5-8 year breeding program works. The USDOE "Forecast 2000" indicated a conservative cost of diesel at \$1.45 to \$1.49 for transportation grade diesel fuel in 1993-5. Therefore safflower may be an economic diesel alternative, substitute or extender. Plant oils would be used to fuel diesel locomotives, freeing conventional diesel stocks for agriculture and other transportation needs. This strategy simplifies the technical problems of converting to plant oil fuel since the number of engine types is minimized.

One significant problem confronting diesel fuel use of plant oils or derivatives (such as monoesters of the parent triglycerides) is lubrication oil contamination. Unburned fuel that blows by cylinder wall/piston ring seals mixes with crankcase lubrication oil, altering its physical and chemical properties. Lube oil thickening and loss of alkaline reserve are commonly observed when engines are operated for extended periods with plant oil fuels, forcing shortened drainout cycles and risking accelerated engine wear. Oxygen-induced polymerization and acid-forming oxidation reactions, largely taking place at points of unsaturation in plant oils or monoesters, are probable causes of viscosity increase and loss of alkalinity (2,3).

Addition polymerization reactions involving unsaturated monomers such as plant oil triglycerides can be catalyzed by trace acid levels or can be due to a free radical mechanism which is independent of acidity. The fact that oxygen can promote such reactions can be consistent with either mechanism since oxygen-double bond reactions can yield acidic species or hydroperoxides that decompose to free radicals (4). Further complicating the mechanism issue is the observation that copper can catalyze polymerization of plant oil triglycerides. Copper is among a group of common metals that show up in used diesel lubrication oil due to engine wear. Other metals in this group that may also have catalytic properties are iron, lead, silver and aluminum.

In the work reported here the lubrication oils studied are SAE 30 base stocks without additives and truck/tractor commercial oils. These oils were selected for the present research because a body of earlier data existed for them. Major findings are tested with 45-weight locomotive oil, but a detailed study of this latter lubricant is the subject of future research.

RESEARCH OBJECTIVES

The general goal of the present research is to develop an understanding of the fundamental problems of plant oil fuel contamination in diesel engine lubrication oil. This understanding should provide a basis for solution of the problems. Specific objectives of the research are listed below.

1. Determine the effects of system variables such as temperature, presence of oxygen and level of plant oil contamination on lubrication oil thickening.
2. Evaluate a selected group of Montana-grown plant oils and plant oil derivatives as contaminants in lubrication oil at a standardized set of exposure conditions.
3. Determine the basic chemical mechanism by which the triglyceride polymerization proceeds.
4. Develop an understanding of the role of metallic catalysts, especially copper, in the polymerization of plant oil triglycerides.
5. Develop a technical basis for chemically inhibiting polymerization of plant oil triglycerides and for deactivating metallic catalyst species.

EXPERIMENTAL DESCRIPTION

Materials

The sunflower oil used in this study was mill grade obtained from Continental Grain Company of Culbertson, Montana. Iodine value for this oil was 140 and the oil was centrifuged to remove visible solids before use. Other oils and derivatives were obtained from a variety of commercial and Montana State University (MSU) sources. Lubrication oil in most experiments was API CD SAE 30 obtained from Phillips Petroleum Company. Base stock 30-weight oil with no additives was also obtained from Phillips. Diesel locomotive oil designated SAE 45 13 TBN was obtained from Burlington Northern (BN).

A variety of chemical additives were investigated in the course of this work. Their descriptions and sources will be identified in the Results and Discussion section. Copper metal foil used in most experiments was 0.125 mm thick and +99.9% purity. All other chemicals used were reagent grade.

Apparatus and Procedures

A new experimental apparatus for testing oil mixture exposures to temperature, oxidation and catalytic surfaces was constructed for this project. The apparatus was designed to roughly simulate the environment of a diesel engine crankcase and oil distribution system. Thermal stability of the paraffinic heater bath oil limited

temperature to 150 C, but this maximum value was judged to be a reasonable compromise between cylinder wall and diesel crankcase reservoir temperatures. The bubbling of preheated gas through the test oil mixtures provided agitation and the presence of oxygen when desired.

Lubrication oil diluted with plant oils or derivatives was exposed to conditions simulating an engine crankcase in 1000 ml four-neck resin flasks as shown in Figure 1. Most work reported herein used 5.0% by weight sunflower oil in lube oil at a total mixture volume of 500 ml. Resin flasks were immersed in an insulated oil bath (Figure 2) generally maintained at 150.0 ± 0.5 C. Preheated oxygen or nitrogen was percolated through oil mixtures using 30 mm fritted glass disks centered at the bottom of the flask. Gas flow was set at 120 ml/min using a Varian Aerograph soap film meter. Metallic copper catalyst was provided as a 2.0 cm x 5.0 cm foil strip formed into a 1.6 cm diameter cylinder which was mounted just above the fritted glass disk. Copper was polished and cleaned with hexane and acetone before use.

Primary measures of deterioration were changes in oil mixture viscosity, alkaline reserve and lubricity. Viscosity was measured in a constant temperature water bath at 40.0 ± 0.1 C with modified Ostwald-Fenske viscometers using ASTM Standard Method D-445/446. Alkaline reserve was determined by ASTM Standard Method D-2896, a potentiometric titration yielding a total base number (TBN). Lubricity of degraded oil mixtures was assessed by ASTM Standard Method D-4172 employing a four-ball wear tester.

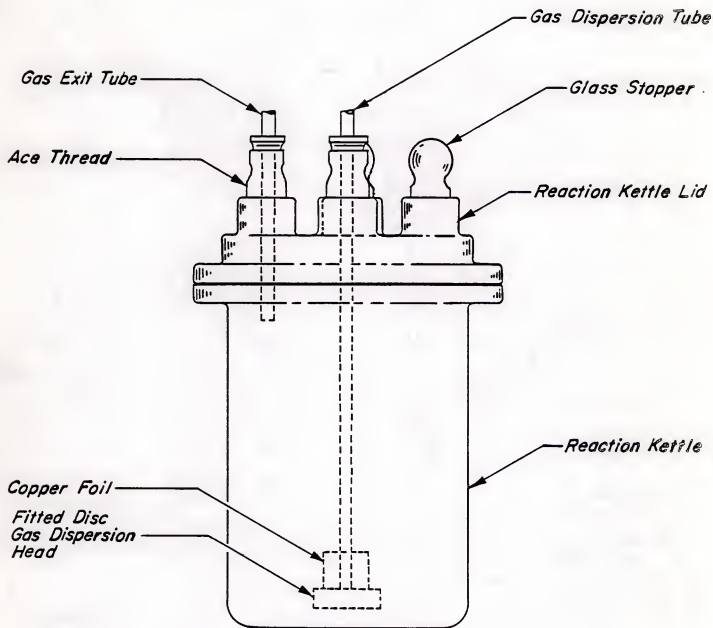


FIGURE 1

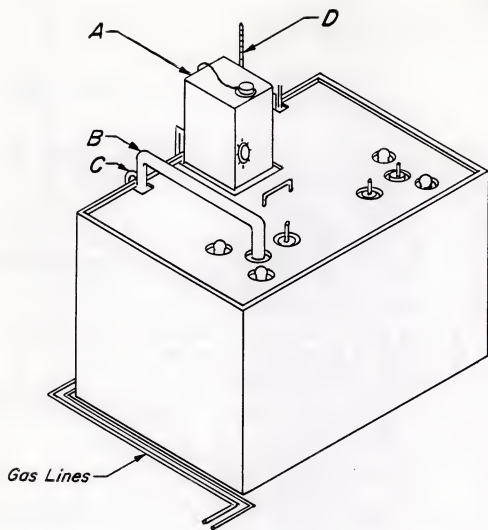
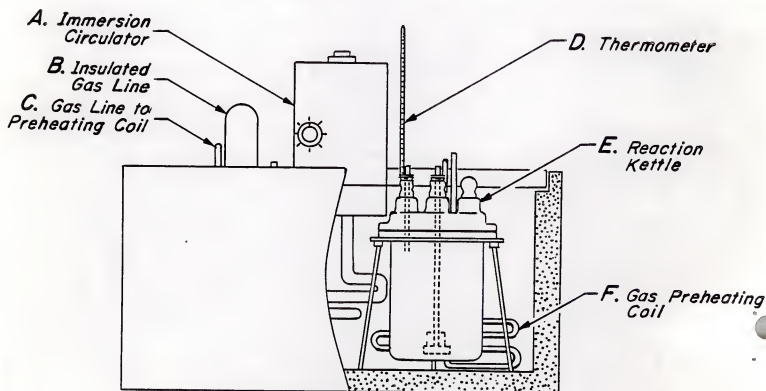


FIGURE 2



Viscosity and total base number testing were run routinely in our current research, and wear testing was performed in an outside vendor facility (Phoenix Chemical). All tests show good precision in replicate analyses.

Analyses for dissolved trace metals were conducted by atomic emission spectroscopy at Case Lubricant Analysis Service. The technique employed total sample conversion to a plasma and was judged to be independent of sample viscosity. Precision for this technique is estimated to be +25%.

RESULTS AND DISCUSSION

A wide range of exposures of lubrication oil contaminated with plant oils or derivatives to conditions simulating a diesel engine crankcase environment was investigated in the course of this work. Much of the detail of this work is reported in Milestones #1 through #5 (appendix pages A-1 to E-8) in the appendix. A summary of results is presented here with reference to figures in the milestone reports.

Impact of System Variables (Milestone #1)

A study of key system variables was conducted to provide a technical framework for the overall project and to help with equipment design. This first work was conducted in 50 ml test tubes with copper present as a fine wire wrapped around the gas dispersion head. Results of this phase of the work aided design of the apparatus of Figures 1 and 2.

Copper presence was investigated briefly in the original apparatus to confirm its importance in the lube oil thickening problem as reported by Bauer et al.(5). A more detailed discussion of the role of copper catalyst is given later in this report. Figure 1 (A-8) gives viscosity versus time for a standard exposure of 5.0% sunflower oil at 150 C for three different levels of copper. Oxygen flow is 2,000 ml/hr in each case. Copper is obviously a catalytic material, and 20 cm of copper wire was selected as a reference level for further studies.

Next oxygen flow rate was varied to test the impact of this variable and the need for precise control of flow rate. Figure 2 (page A-9) gives viscosity rise results at 150 C for oxygen flow of 4000 ml/hr with two levels of copper. For comparison the dashed line is 2000 ml/hr oxygen with 20 cm of copper wire. Oxygen flow rate is clearly a key variable that requires precise control of flow. Not shown in this figure is the finding that nitrogen flow at any rate causes no discernible viscosity rise. A rate of 2000 ml/hr oxygen was selected as a standard for further work in the original test tube studies.

Next, various concentrations of plant oil contamination were studied at 150 C. Contamination levels of 1%-50% plant oil in lubrication oil have been considered in the literature (1) with levels of 1%-10% estimated in actual engine trials. Figure 3 (page A-10) shows the response of viscosity rise to level of sunflower oil contamination with 2000 ml/hr oxygen and 20 cm copper wire. As expected, uncontaminated lubrication oil does not thicken, and the rate of polymerization corresponds strongly to the concentration of plant oil. A somewhat arbitrary contamination level of 5.0% plant oil or derivative was selected as a reference level for the present research.

A reference set of lube oil exposure conditions was established for the test tube apparatus. These conditions are 5.0% sunflower oil in SAE 30 lubrication oil at 150 C with 2,000 ml/hr oxygen percolation rate and 20 cm copper wire. These conditions yield the middle curve of Figure 1

(page A-8) for viscosity rise. Later in the work as experiments shifted to the newer flask apparatus, the oxygen flow was changed to 7,200 ml/hr, and a 2.0 cm X 5.0 cm copper foil strip was be used to better adapt to the new volume and flask geometry.

As ASTM rule of thumb for oil failure due to thickening is a 375% increase. The reference curve of Figure 1 (page A-8) shows that viscosity, with 20 cm copper catalyst rises from about 100 centistokes (cSt) to 475 cSt in 45 hours. Thus, the contaminated mixture in this experiment "fails" in 45 hours of simulated exposure.

Once the reference conditions based upon viscosity rise were selected, their impact on oil mixture alkalinity loss was assessed. Figure 7 (page A-13) shows the loss of alkalinity with time for the reference set of conditions. Total base number (TBN) drops sharply at about 20 hours, roughly the same time at which viscosity rise accelerates. This correspondence leads one to suspect a relationship between alkalinity (acidity) and polymerization - more on this topic later in the mechanism section of this report.

In Figures 8 and 9 (pages A-14 and A-15) alkalinity losses for 4,000 ml/hr oxygen flow and no copper catalyst are given along with a dashed curve for the reference case from Figure 7 (page A-13). These departures from reference conditions have little impact on TBN loss rate, if any at all in the case of 4,000 ml/hr oxygen. It is especially notable that TBN still falls off quite sharply when copper is absent, while polymerization is very slow in the absence

of copper. It appears from this that deactivating copper as a polymerization catalyst might not affect alkalinity loss.

A final topic of this first phase of the research is the question of loss of lubricity as contaminated lube oil polymerizes and acidifies. To test this parameter, degraded oil mixture samples from a reference exposure were collected over a range of viscosity and then analyzed for lubricity. The four-ball wear test of ASTM D-4172 illustrated in Figure 11 (page A-17) gave the scar results of Figure 12 (page A-18) as a function of viscosity. Scar diameter is little influenced by viscosity over the 100-500 cSt range. Thus, oil mobility and not lubricity seems to be a key in the problem of lubrication failure due to oil thickening.

Comparison of Fuel Candidates (Milestone #2)

The second phase of the research investigated several plant oils and derivatives other than sunflower oil for possible use as diesel fuel. This study was intended to check for differences between sunflower oil and other vegetable oils and help guide plant breeding activities on other oils, especially safflower.

Figure 1 (page B-6) gives viscosity rise results for safflower and rapeseed oils at reference conditions in the 50 ml test tube apparatus along with the sunflower results (dashed curve) discussed previously. All oils are at 5.0% concentration. Iodine values for the safflower and rape oils are 130 and 120, respectively, compared with 140 for sunflower oil. The differences seen in Figure 1 (page B-6)

are slight, indicating that viscosity changes probably are about the same for all of them.

Alkalinity loss curves for the three Montana-specific plant oils are presented in Figure 2 (page B-7) again with the sunflower curve from Figure 7 (page A-13) given as a dashed line. A more rapid loss of alkalinity is depicted for the safflower and rapeseed oils, but a qualification is needed here. The sunflower result was obtained using a titrimer which subsequently failed. The results for the other two oils were obtained with a new titrimer and the difference seen in Figure 2 (page B-7) may be due to this switch of equipment. The more rapid loss of alkalinity for the safflower and rape oils is not in line with their iodine values versus that for sunflower. Whatever the exact case, alkalinity losses among the three oils does not indicate that any of them is clearly better than the others.

Three transesterified plant oil esters were evaluated at 5.0% in much the same way as the three plant oils. These esters were methyl and ethyl sunflower and methyl rapeseed. The iodine values for methyl sunflower and methyl rapeseed were found to be 140 and 115, respectively. No value was obtained for ethyl sunflower because not enough of it was available. Viscosity increases for the three esters are shown in Figure 3 (page B-8). The methyl sunflower result is a dashed curve with specific data points given in Figure 6 (page A-12). Viscosity rises in Figure 3 (page B-8) are not large, certainly far smaller than those for the original plant oils. It would seem that these esters might be

significantly better fuel choices based upon the need to avoid lube oil thickening. However, in all three cases important quantities of gel-like precipitates were observed in the oil mixtures. It seems likely that these gels are insoluble forms of polymerized esters, and thus the viscosity rise curves are deceptively low. Insoluble gel is at least as troublesome a problem as thickening disrupting lube oil distribution in a diesel engine.

Loss of alkalinity for the three esters is shown in Figure 4 (page B-9). The methyl sunflower result is again a dashed curve from an earlier figure - Figure 10 (page A-16). The three curves differ little in form, although the ethyl sunflower curve does have a distinctly lower initial TBN value. This may be due to the age of this sample and the possibility that it may have become more acidified over time. In any case no single ester fuel is clearly superior on the basis of alkalinity. Nor are the alkalinity loss curves for these esters notably different from those for the plant oils of Figure 2 (page B-7).

Results of this phase of the research show that all fuel candidates pose serious problems for the lubrication system of a diesel engine. Solutions to the viscosity, gel and alkalynity problems must be found before any of these materials can be useful as diesel fuel.

Chemical Mechanism Study (Milestone #3)

Early in this research, the mechanism operating in the formation of high polymers through triglyceride chain

reactions in a dilute oil mixture, was not clear. Both ionic and free radical initiated mechanisms have been proposed in the literature, with the case of pure state polymerization almost certainly a free radical mechanism (4). It is important to know the chemical mechanism for the polymerization of plant oil/lube oil mixtures in the present work to help guide chemical additive approaches to the thickening problem.

At the outset of this project it was envisioned that hydrocarbon base stock with no stabilizing additives would be used as the lube oil to avoid the complexity of possible interactions with the unknown chemical additives in commercial SAE 30 lube oil. However, all attempts to use the base stock lubricant contaminated with sunflower oil produced heavy gel precipitation - results that were very difficult to use for quantitative comparisons. Attempts to run at lower temperature with higher concentrations of sunflower oil to get viscosity rise without gel formation all failed. Thus, the mechanism study was conducted at the same reference conditions used with SAE 30 commercial oil. Fortunately the mechanism study seemingly yielded a clear result in spite of the presence of unknown additives in the lube oil.

A. Ionic Polymerization Study

The presence of acids, and hence H^+ ions, can catalyze addition polymerization under some conditions. The first phase of the present mechanism study looked for evidence that ionic catalysis is a factor in the polymerization of

plant oil contaminants in lubrication oil. Alkalinity loss measurements indicated acid generation during standard exposure testing of contaminated lube oil, leading to speculation that ionic (acid) catalysis plays a role in plant oil polymerization under the conditions used in this research.

Initial trials to test for ionic catalysis involved adding phosphoric acid to a level of 3.0% at the beginning of a standard trial with 5.0% sunflower/SAE 30 at 150 C. Immediate total base number (TBN) values were erratic, but at 12 hours the TBN value was 0.18 mg KOH/g, indicating little alkaline reserve. The viscosity rise behavior for this phosphoric acid trial is given in Figure 1 (page C-10). Also given in Figure 1 (page C-10) is the standard 5.0% sunflower/lube oil response with no added acid.

Figure 1 (page C-10) shows that free mineral acid does not accelerate plant oil polymerization over 40 hours of exposure. The two curves are very nearly the same, with the standard trial actually polymerizing somewhat faster. Thus, there is no evidence of ionic catalysis in this trial.

Since ionic catalysis might operate with only small quantities of free acids and be insensitive to excess amounts, it was decided to test the indication of Figure 1 (page C-10) in a reverse manner; i.e., maintain TBN at a high value and test for reduced polymerization. To accomplish this, an alkalinity maintenance additive, Amoco 9231, was used. This compound, an overbased calcium

phenate, was added periodically to a standard 5.0% sunflower/lube oil trial to keep alkaline reserve up and simultaneously measure extent of polymerization.

Results of the alkalinity maintenance trial with Amoco 9321 are given in Figure 2 (page C-11). Points in time where TBN ascends vertically correspond to additions of the additive. Normally (without the additive) TBN falls to approximately 2.0 at 40 hours exposure. Here TBN averages near 6.0 for the entire exposure. A comparison of viscosity rise in the present case with the standard response (no additive, dashed line) again fails to show any ionic catalysis impact. Clearly, free acid content is reduced, but polymerization proceeds at a normal pace.

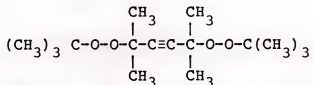
The results of Figures 1 and 2 (pages C-10 and C-11) rather conclusively show that ionic catalysis plays at most a minor role in polymerization of plant oil contaminants in the lube oil. It is possible that unknown additives in the lube oil mask the ionic catalysis impact, but this seems unlikely.

The trial using Amoco 9321 as an alkaline agent is quite significant from the standpoint of alkalinity maintenance. Figure 2 (page C-11) demonstrates that this agent can be used to avoid excess acidity (and hence corrosion) by making periodic additions to the lubrication system. Thus, even if attempts to block acid formation in later research are unsuccessful, a route to maintaining alkaline reserve is known using a commercially available material.

B. Free Radical Study

With an ionic polymerization mechanism apparently ruled out of consideration, work focused on a free radical pathway. Oxidation of double bonds to form acids and other carbonyl compounds is known to proceed by this route (6). Addition polymerization of unsaturated compounds, especially polyunsaturated compounds, can also proceed by a free radical mechanism. Mechanism details can be quite complex as summarized by Wexler (4), but all such mechanism pathways involve oxidation or additive chemicals that directly decompose to yield free radical intermediates that then initiate polymer chain reaction.

The reference case exposure of contaminated lube oil used in this research involves percolation of oxygen through 5.0% sunflower mixtures at 150 C. To test whether a free radical mechanism is involved in the polymerization, continuous oxygen bubbling was eliminated from the routine and replaced by periodic additions of Lupersol 130, a free radical generator. Lupersol 130, a Lucidol Pennwalt organic peroxide product, has the structure



This compound is known to cleave between oxygen atoms to yield free radicals with an estimated half life of 57 minutes at 150 C.

Figure 3 (page C-12) gives results for two trials where Lupersol 130 was added every 2.5 hours to a 5.0% sunflower/lube oil system. Addition levels were 0.5% and 0.1%. Also shown in Figure 3 (page C-12) as a dashed line is the standard case with oxygen percolation. It is seen that the magnitude and general shape of the standard viscosity rise curve can be reproduced with the peroxide additive and no oxygen. This is strong evidence that the reference case polymerization (viscosity rise) results from an oxygen-induced free radical mechanism.

Once it is known that a free radical mechanism governs the triglyceride polymerization, an obvious approach to mitigating the reaction is to employ free radical inhibition compounds which consume free radicals before they can initiate the chain reaction. However, it was also known that copper, and perhaps other engine wear metals, catalyze the polymerization thickening of triglycerides. Before attempting to block the general polymerization reactions, it was decided to investigate the role of metallic catalysts in triglyceride polymerization and then bring this knowledge to bear on the overall oil thickening problem.

Copper Catalysis Study (Milestones #3 and #4)

The copper catalysis phase of this research was conducted in the newer apparatus described in the Experimental section. The 20 cm copper wire in earlier work was replaced by 2.0 cm x 5.0 cm foil strips mounted over the percolation frit in the 1000 ml resin flask.

Another change from earlier work involved a switch to a different commercial lot of SAE 30 lubrication oil. This oil met all required specifications for this type of oil but contained a different set of additive chemicals as determined in atomic emission spectroscopy analyses. Again, the overall composition of these additives was unknown.

Reference viscosity rise curves for 5.0% sunflower oil in the new lot of commercial oil at 150 C are given in Figure 3 for no copper and the standard 2.0 cm x 5.0 cm strip of foil. These curves rise faster than earlier reference cases, undoubtedly due to the change in the oil additive package. These new curves in Figure 3 now become baselines for the catalysis work.

First, four other common wear metals were tested for catalytic activity at the conditions of this work. These metals were aluminum, lead, silver and iron. All show up in analyses of degraded diesel engine oils. All metals were tested as 2.0 cm X 5.0 cm foil strips just as with copper. None of these metals showed any catalytic activity with each trial approximating the no-copper case. Thus, it appears that a study of copper alone is sufficient to assess metallic catalysis.

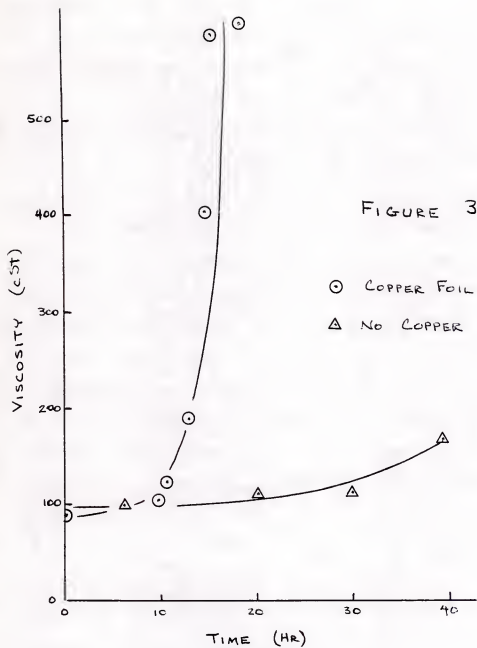
The mechanism(s) of copper catalysis of triglyceride polymerization is far from resolved. Several suggested autoxidation mechanisms (7,8) involve ionic copper species, presumably dissolved. To check copper dissolution in the present work degraded oil mixture samples were taken at the completion of each trial of Figure 3 and subjected to atomic

emission spectroscopy. Results were 0 ppm and 5 ppm copper for the no-copper and copper foil trials, respectively. Thus it appears that copper foil dissolves in the oil mixture in trace amounts, and these dissolved species may contribute significantly to the catalytic effect.

At this point in the research the relative catalytic contributions of copper as surface and as dissolved species were unknown. To gain insight on this matter a standard case experiment was conducted where the copper foil was initially present but was removed at four hours, a time at which only slight viscosity rise is observed in Figure 3. Thereafter, the experiment was taken to conclusion without the presence of copper surface. Results for this experiment are given in Figure 4 along with the curves of Figure 3 shown as dashed lines for reference.

The viscosity rise for the copper removal trial of Figure 4 nearly matches the curve for the case where copper foil is present throughout the experiment. If copper surface is a primary catalytic factor, it must play its role initially and be of little consequence thereafter. On the other hand, if soluble copper species dominate the catalysis, a sufficient quantity of such species must evolve early in this experiment.

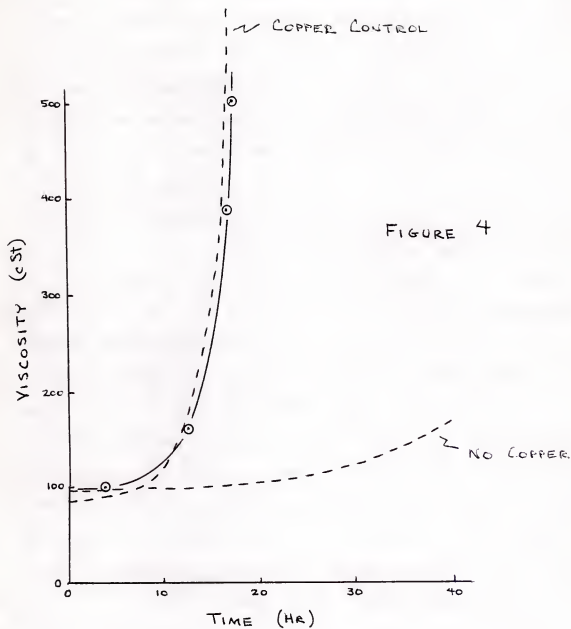
Several related experiments presented in Figure 4 (page C-13) confirm the catalytic activity of dissolved copper in the present system. In each of two experiments 2.0 cm x 5.0 cm copper foil strips were exposed to lube oil only for 48 hours at 150 C in the resin flasks. In one case oxygen was



percolated through the single oil and in the other nitrogen, both at the standard 120 ml/min. At 48 hours the copper strips were removed and sunflower oil was added to the flasks to yield 5.0% mixtures by weight. Also at the 48 hour mark the nitrogen cell was switched to oxygen flow at the same rate, and both cells were then continued at 150 C to yield the results of Figure 4 (page C-13).

Figure 4 (page C-13) presents the viscosity increases for the two experiments under consideration with the 48 hour mark designated as time zero. Also shown as a dashed line is the reference case curve where copper foil is continuously present from the beginning (from Figure 3). The ensuing viscosity rise for the case where copper foil was first "soaked" in lube oil with nitrogen is the greatest of the three curves of Figure 4 (page C-13) with the standard case and the oxygen extended trial following in declining order. Clearly, sufficient copper is present in all three cases to catalyze the triglyceride polymerization, and in the extended trials this copper must be dissolved since the copper foil was removed prior to introducing sunflower oil into the system.

For the two extended trials of Figure 4 (page C-13) samples of the lube oil were taken at 48 hours for dissolved copper testing by atomic emission spectroscopy. Results were somewhat surprising at 14 ppm and 28 ppm copper for the nitrogen and oxygen pretreatments, respectively. It is interesting to note that the nitrogen pretreatment gave the greater viscosity rise while having only half the dissolved



copper of the oxygen pretreatment trial. There are a number of possible explanations for this observation, and resolution of this issue is the topic of ongoing research. Oxygen may be facilitating copper dissolution by the production of carboxylic acids which then attack the metal surface yielding copper salts having some solubility. Copper oxides may also be forming at the conditions of this work. Whether these copper salts and oxides would be as active catalytically as other dissolved copper species generated during the nitrogen pretreatment phase of the second trial is unknown, but the activity of the latter dissolved species appears to be greater.

Next a set of experiments was run to retest the homogeneous catalysis of sunflower triglyceride polymerization by dissolved copper in the present system, but with a different source of copper. A copper complex, cupric acetylacetonate, was selected for testing as a soluble copper catalyst. This complex, which is generally quite soluble in organic systems (9), appeared to dissolve readily at 1.0% in the 5.0% oil mixture at room temperature. The thermal stability of cupric acetylacetonate at 150 C is unknown, but similar metal complexes seem to exhibit at least moderate stability at such temperatures.

Figure 5 (page C-14) gives viscosity rise results for three experiments testing cupric acetylacetonate as a homogeneous catalyst. Sunflower oil at 5.0% and oxygen percolation were present throughout the trials, but copper foil was absent. A dashed curve again gives the reference

copper foil case from Figure 3. Copper concentrations are expressed as added copper by weight. Figure 5 (page C-14) shows again that soluble copper can indeed catalyze autoxidation of the plant oil triglycerides at conditions of this work. It is interesting to note that the 5 ppm and 10 ppm curves closely match the reference copper foil case in form and magnitude, a significant finding recalling the reference case gave 5 ppm copper at its termination. The trial with 5 ppm added copper yielded an atomic emission spectroscopy result of 5 ppm at its conclusion, seeming to confirm both the stoichiometry and analytical techniques.

Although the exact pathway(s) for autoxidation of plant triglycerides to yield high polymers is uncertain, there seems wide agreement that the formation of intermediate hydroperoxides and their decomposition to yield free radicals are integral to the mechanism (4). However, it is unknown whether copper catalyzes either of these steps. An attempt to shed light on this issue was made by replacing oxygen with nitrogen in a standard 5.0% sunflower oil exposure at 150 C and by making periodic additions of the commercial diperoxide Lupersol 130.

Two trials using Lupersol 130 with and without the continuous presence of copper foil are shown in Figure 5. The peroxide was added to the oil mixture at 1.0% every 1.5 hours, and good mixing was assured by the nitrogen bubbling action. The periodic additions of the peroxide were again based upon its decomposition half-life of approximately 57 minutes at 150 C.

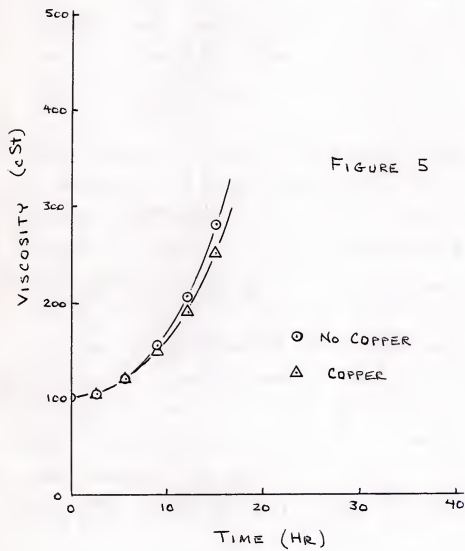
The two curves of Figure 5 are essentially the same with the presence of copper having no apparent impact on the rate of polymerization. This result indicates that copper does not catalyze peroxide decomposition, since higher addition levels of Lupersol 130 with attendant higher yield rates of free radicals are known to cause more rapid polymerization. It thus appears that the catalytic role of copper in this system may involve the hydroperoxide formation reaction or perhaps direct interaction with oxygen to yield free radical species which initiate the triglyceride chain reactions.

Inhibition and Deactivation Studies (Milestones #4 and #5)

The prior research identified a free radical chemical mechanism and the importance of catalytically active soluble copper species. Both facets were addressed in attempts to slow the unwanted polymerization reactions of the sunflower oil triglycerides.

The first step in the mechanism of free radical addition polymerization involves oxygen attack at points of unsaturation (double bonds) in the triglyceride oil (4). The initial result of this oxidation is creation of unstable hydroperoxides. The hydroperoxides spontaneously decompose to yield free radical species which then attack points of unsaturation in other plant oil molecules and thus propagate the addition chain reaction.

A widely used antioxidant, zinc dialkyl dithiophosphate (ZDTP), was tested first as a polymerization inhibitor. This product is speculated to inhibit oxidation of motor



oils by converting hydroperoxides to non-radical products. ZDTP was added at 1.0% to a mixture of 95% base stock lube oil/5% sunflower oil. The use of hydrocarbon base stock as the lube oil substrate is practically required if an understanding of the system chemistry is sought. This is due to the unknown chemical nature of the additive package in commercial oil. Standard conditions of 150 C, oxygen percolation and presence of copper foil catalyst were employed. The result of this trial is shown in Figure 1 (page D-8) along with a control experiment (dotted line) where no ZDTP was used.

Figure 1 (page D-8) shows that there was no appreciable rise of viscosity in either case, with or without ZDTP. However, in each case a great deal (perhaps 10% by volume) of insoluble gel was found on the walls and other surfaces of the exposure vessel. This gel appears to be polymerized plant oil swollen by lubrication oil but not soluble in it. The difference between this gel formation in base stock oil and the viscosity build-up in commercial SAE 30 lube oil is surely due to chemical additives present in the commercial oils. It was decided to continue the inhibition study with base stock oil and attempt to block gel formation. Any success would then be tested in contaminated commercial lubrication oil.

Another antioxidant, zinc diamyl dithiocarbamate (ZDTC) was next tested as a polymerization inhibitor. This compound is also speculated to produce non-radical species from unstable hydroperoxide intermediates. The manufacturer

of ZDTC, Vanderbilt Corporation, also suggests that the ZDTC can inhibit polymerization by terminating the chain reaction through destruction of free radicals. Vanderbilt also suggests that ZDTC may deactivate metallic polymerization catalysts.

Figure 2 (page D-8) gives the viscosity rise results for the use of ZDTC at 0.5% and 1.0% in the 95% base stock/5% sunflower oil mixture. Again no appreciable viscosity rise is observed, but in these cases no sludge was formed until nearly 40 hours exposure, and beyond this point sludge formation was only slight. The standard conditions of 150 C, oxygen percolation and copper foil catalysts were employed in these trials.

Clearly, the addition of ZDTC yields a breakthrough in inhibiting the degradation of sunflower oil in a lube oil mixture. In all other trials with commercial or base stock lube oil at standard conditions, sunflower oil degradation was observed as either rapid viscosity rise or excessive sludge formation. The zinc diamyl dithiocarbamate seems to be sharply inhibiting the polymerization(s) leading to these degradation effects.

Next ZDTC was tested at 1.0% and standard conditions in a 95% basestock/5% sunflower mixture except oxygen was replaced with inert nitrogen flow and Lupersol 130, the free radical generator, was periodically added as reported earlier. If ZDTC works by scavenging free radicals, it should slow the known polymerization rate with Lupersol 130.

Figure 3 (page D-10) shows viscosity rise data for the Lupersol 130 experiment, with and without the use of 1.0% ZDTC. The results are similar, but the trial with ZDTC shows a somewhat reduced viscosity rise. The ZDTC may be inhibiting polymerization by partially blocking the decay of Lupersol 130 into free radicals or perhaps by consuming some free radicals as they are formed. Whatever the effect of ZDTC, it is not pronounced when tested in conjunction with a non-oxidative free radical generator.

Of significant interest in Figure 3 (page D-10) is the fact that gel was essentially absent in both trials while the viscosity increases were greater than in any trial in which significant gel was formed. This result is significant and helps form the basis for a theory of gel formation as discussed later in this report.

Zinc diamyl dithiocarbamate was next tested at 0.5% and 1.0% in a standard exposure trial using commercial lube oil in place of the base stock. Oxygen and copper catalyst were used as normal. Results of these trials are shown in Figure 4 (page D-10). The trials with differing ZDTC levels are practically identical, but both show a distinct inhibition of viscosity rise compared with a control experiment containing no ZDTC. Although ZDTC forestalls the viscosity rise for 10-12 hours, it is not nearly as effective in inhibiting viscosity rise as it is in minimizing sludge formation in hydrocarbon base stock experiments. Perhaps some unknown additive in the commercial lube oil is

deactivating the ZDTC or is promoting polymerization by a mechanism(s) not fully inhibited by ZDTC.

Next ZDTC at 1.0% was used in the 95% base stock/5% sunflower mixture with 5 ppm cupric acetylacetomate (CAA) replacing copper foil catalyst. The viscosity rise was practically nil, and just as with copper foil, gel formation was minimal out to 50 hours exposure. This result indicates that ZDTC does not deactivate the metal surface, and further indicates that the primary role of ZDTC is inhibition of free radical initiation.

Zinc diamyl dithiocarbamate was tested at 1.0% at standard exposure conditions - 5.0% sunflower, 150 C, copper foil catalyst, oxygen percolation - in 45-weight diesel locomotive base stock oil. This base stock oil is a hydrocarbon mixture with no stabilizing additives. Viscosity increases seen in this trial are shown in Figure 1 (page E-8) along with the corresponding results for 1.0% ZDTC with SAE 30 basestock and 5.0% sunflower.

Figure 1 (page E-8) shows that viscosity rise is not significant for the locomotive base stock trial - an expected result since both base stocks are chemically similar hydrocarbons. Of greater interest is the impact of ZDTC on insoluble gel (polymer) production, as yet an unpredictable aspect of any base stock trial. Arrows mark the onset points of discernible amounts of insoluble gel in the two experiments presented in Figure 1 (page E-8) Gel is present at 32 hours in the locomotive trial, but its onset is not until 50 hours in the SAE 30 case. The precision of

this difference is uncertain, but the difference may be important if oil drain-out cycles in locomotives fall within the general range of these trials.

Finally, two other proposed addition polymerization inhibitors were tested in standard trials using a 95% hydrocarbon basestock/5% sunflower mixture. These compounds were Vanlube 81 (Vanderbilt) and Ethanox 702 (Ethyl Corporation) and each is supposedly active in consuming free radicals and thus inhibiting the propagation step of polymerization. Vanlube 81 is a dioctyl diphenylamine and Ethanox 702 is 4,4' methylene bis (2,6 ditertbutyl phenol). Neither of these additives showed any inhibitory strength, each essentially showing the inactive behavior of ZDTP in an earlier trial.

A search of the literature (10) revealed a large number of compounds that show some deactivation properties for metal polymerization catalysts. These compounds tend to contain phosphorous, sulfur or nitrogen in various combinations and presumably either poison or sequester metals to render them inactive.

Only one compound from the search for metal deactivators has been able to show any distinct retardation of polymerization. The compound is N, N' disalicylidine-1,2 propane diamine (NNPD) from Dupont, and it is designed to specifically deactivate copper species. Figure 2 (page E-8) shows the impact of NNPD on viscosity rate of rise at three addition levels (75% active NNPD in xylenes). The dashed line is the standard case - copper foil, 5.0% sunflower, 150

C, oxygen flow - with no NNPD. Obviously the additive retards polymerization, but whether metal deactivation is the primary mechanism is not certain. The reason for the doubt is that the viscosity rise curve for 1.5% NNPD is actually slower than the no-copper case for this same system. The NNPD is doing more than just deactivating copper at this level - it is probably acting as an antioxidant also.

Specialty compounds such as NNPD are not yet produced in bulk by Dupont, but a projected commercial selling price in bulk is \$4.14/lb. The corresponding price for ZDTC is estimated to be \$1.30/lb. At these prices, the compounds (or others like them) must be effective at low concentrations to control lube oil cost at reasonable levels. The additives may substitute for other costly deactivators already present in a commercial "package," thus minimizing added cost.

Clearly, additives that show benefits separately such as ZDTC and NNPD may yield synergism when combined. However, the individual mechanisms are not well understood, and any combined effects would be even less understood. Thus, continued research will deal with the individual additives until meaningful conclusions can be drawn from their combination.

Insoluble Gel Characterization (Milestone #5)

The nature of insoluble gel and its relation to viscosity build-up must be understood before it can be

minimized and before additive-free base stocks can be used for further work. Several experiments were conducted to determine whether this gel is merely an insoluble linear polymer or a more complex, perhaps crosslinked, chemical species.

Insoluble gel from an SAE 30 base stock trial was decanted from supernatant and then mixed at 5.0% in SAE 30 commercial lube oil. The mixture was heated with agitation to 150 C and held for 10 hours. Throughout the test the mixture was examined for evidence of gel dissolution. There was no discernible loss of solid gel, although there was a definite softening. This result seems to show that the gel is not the same chemical species that causes viscosity rise in the commercial oil. It was surmised that the materials might be the same and that lack of a dispersant in basestock oil leads to a precipitated solid polymer form.

Gel swollen with base stock oil was next subjected to high speed comminution in a laboratory blender in an attempt to form a thickened homogeneous liquid phase. Blending for intervals up to 105 minutes failed to produce homogeneity. This second failure to produce a true solution or even a colloidal dispersion by physical means again indicates that gel may not be the same material that causes viscosity rise in commercial SAE 30 experiments.

Finally, a widely used industrial oil dispersant Paronox 107 (succinimide-based) was tested in an attempt to disperse gel in base stock oil at 150 C. No apparent loss of solid phase was noted throughout this extended test at 150 C.

Once again a thickened liquid phase was not achieved.

The general conclusion of the three experiments cited above is that the insoluble gel formed in sunflower/base stock experiments is fundamentally different from the soluble polymer that produces viscosity build-up in sunflower/commercial lube trials. The gel polymer may be insoluble due to crosslinking or possibly due to being more polar than the lubrication oil. This latter concept is new but seems promising at this time. It is hypothesized that acid and other carbonyl groups formed by oxygen attack at double bonds in high polymer molecules give these molecules sufficient polarity to cause them to be insoluble in the non-polar lube oil. Gel forms in base stock, perhaps because it contains no antioxidants intended to suppress acid formation. Acid formation may be suppressed in commercial lube oils that contain antioxidants, such that polymerized plant oils remain soluble and this polymer then manifests itself as increased viscosity.

Scouting trials using octadecyl amine (ODA) as an additive supports the polar gel theory hypothesized above. When ODA is periodically added to a reference exposure using base stock there is no gel formed, and viscosity rises in the same way as with commercial lube oil. The ODA may react with acids to form less polar, soluble amides in the polymer sidechains, and hence a viscosity rise is observed. Further testing of this approach to eliminating gel will be a focus of continued research on the lube oil problem.

CONCLUSIONS

1. System variables that have a major impact upon the thickening of diesel lubrication oil contaminated with plant oil fuel are temperature, level of plant oil contamination, presence and flow rate of oxygen, and presence of copper. Thickening increases with increases in these variables.
2. From the standpoint of diesel lubrication oil degradation there is little basis for selecting a best fuel candidate from among sunflower, safflower and rapeseed oils and three derivative esters. The parent oils yield severe thickening and alkalinity loss, and the esters give rapid gel formation and alkalinity loss.
3. Lubrication oil thickening (triglyceride polymerization) proceeds by a free radical mechanism. Ionic species do not seem to influence the rate of thickening.
4. Copper is a strong catalyst for triglyceride polymerization at conditions of a diesel engine crankcase. Soluble copper species dominate the catalysis. Other common engine wear metals tested show little or no catalytic behavior.

5. Several chemical additives show promise for slowing the thickening of contaminated lubrication oil. Zinc diamyl dithiocarbamate is an effective antioxidant at certain conditions, and N,N' disalicylidine - 1,2 propane diamine shows promise as both a metal deactivator and antioxidant. Inclusion of either of these compounds in a commercial lube oil additive "package" would not substantially alter the system operating cost.

RECOMMENDATIONS

The information and understanding developed in the course of this work are substantial, but further research is recommended.

1. Attempts to use and understand contaminated hydrocarbon base stocks should be a continued research focus. Proprietary chemical additives in commercial lubrication oils pose an overwhelming problem for understanding the system chemistry.
2. The effort to inhibit polymerization and acidification of triglycerides has a promising basis and should be emphasized in future research. The chemical functions of specialty additives such as ZDTC and NNPD must be understood to maximize their efficacy.
3. Ongoing research should seek to understand the key chemical differences between viscosity-forming and gel-forming high polymers. Both are major problems confronting use of plant oils as fuels.
4. Well-designed trials with diesel engines should be conducted in future research to establish a correlation with the simulated laboratory crankcase environment.

TIMELINE AND BUDGET

The original term of grant RAE-84-1040 was January 3, 1984 through February 28, 1986. However, the contract was not signed until early March, 1984. Amendment No. 1 to RAE-84-1040 was adopted February 3, 1986 to extend the term of the contract until August 30, 1986. All required milestone reports and this final report are complete prior to that date.

The total budget for this research project is \$87,548 of which RAE-84-1040 contributed \$39,548. Remaining support is being provided by a concurrent \$48,000 grant from Renewable Materials Engineering, Division of Chemical and Process Engineering of the National Science Foundation. All research is being completed within budget limitations.

ACADEMIC AND PUBLICATION RESULTS

All or part of five masters theses (three complete and two in progress) have been supported by RAE-84-1040. Students supported were C. Rewolinski, S. Jette, A. Dutta, J. Keller and R. Raman.

Three refereed publications have resulted from the support and a fourth is in preparation.

1. C. Rewolinski and D.L. Shaffer, J. Am. Oil Chem. Soc., 62, 1120 (1985).
2. C. Rewolinski and D.L. Shaffer, J. Am. Oil Chem. Soc., 62, 1598 (1985).
3. S.J. Jette and D.L. Shaffer, J. Appl. Polym. Sci., in press (1986).

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APPENDIX

"CONTAMINATION OF DIESEL ENGINE LUBRICATION OIL
BY PLANT OIL DERIVATIVE FUELS"

Milestone Report #1

*Experimental Apparatus

A new experimental apparatus for testing oil mixture exposures to temperature, oxidation and catalytic surfaces has been constructed for this project. Apparatus consists of an insulated heating oil reservoir within which two separate 500 ml resin flasks can be located. A resistance circulatory oil bath heater controls reservoir temperature to within $\pm 0.1^{\circ}\text{C}$.

The resin flasks are large enough to allow small oil mixture samples to be removed for destructive testing while long duration experiments continue. Having two flasks in the unit allows two different experiments to be conducted simultaneously. The only factor that must be common in the two experiments is temperature. This is a minor limitation as most experiments will be conducted at 150°C .

Oxygen, nitrogen or other process gases are delivered to the test flasks through stainless steel lines outfitted with precision needle flow control valves. Gas is percolated through sample oil mixtures by immersed fritted glass discs centered at the bottom of the resin flasks. Various configurations of metal catalyst surfaces can be mounted on the glass frits to provide agitated catalyst/oil/gas contacting.

*Preliminary Results - Viscosity Rise

All experimental results collected to date are for systems of mixtures of sunflower oil or its methyl esters in API CD SAE 30 lubrication oil. This latter item is a standard heavy duty lube oil used in diesel truck and tractor engines. Scouting testing of 13TBN SAE 45 medium speed locomotive lube oil basestock yielded unacceptable thermal degradation at a standard temperature of 150°C. A supply of 13 TBN SAE 45 lube oil containing stabilizing additives has just been acquired, and results with this oil will be reported in subsequent milestone reports.

All viscosities reported below are at 40°C as determined in NBS calibrated Canon-Fenske viscometers using ASTM standard method D-445/446.

Effect of Metal Catalyst

Work by numerous researchers into the polymerization or "drying" of plant oils shows the importance of the presence and quantity of metal catalysts. This work will study the fundamentals of catalysis caused by common engine wear metals. Figure 1 shows initial results of the role of copper/iron catalysts on viscosity rise. Here viscosity is plotted against time at 150°C for a 5% sunflower/95% SAE 30 lube oil mixture. Several lengths of metal catalyst wire wrapped on the fritted bubbler were tested, and the influence of the catalyst is clearly significant. In this figure oxygen is percolated through the test mixture at a rate of 2000 ml/hr. A wire length of 20 cm was arbitrarily selected as a basis for testing of other system variables.

Effect of Oxygen Flow Rate

We are certain (again based upon "drying" literature reviews) that oxygen plays a primary role in plant oil polymerization in a diesel engine crankcase. Figure 2 illustrates that role. Here temperature of exposure is again 150°C, and sunflower oil level is 5%, but oxygen flow rate is 4000 ml/min. For comparison, the result using 20 cm catalyst wire at 2000 ml/min is shown as a dotted line on Figure 2. Higher oxygen flow speeds viscosity rise, probably due to combined mass transfer and chemical reaction kinetic effects. Further preliminary testing employs an oxygen flow rate of 2000 ml/min as a basis. Not shown in this figure is the result that viscosity does not rise discernibly when nitrogen at 2000 ml/min is substituted for oxygen.

Effect of Plant Oil Contamination Level

Figure 3 shows the response of viscosity rise to level of sunflower oil contamination in SAE 30 lube oil. Clearly plant oil concentration is a major factor in the problem of thickening crankcase oils. Again, temperature is 150°C with catalyst and oxygen flow fixed at basis levels. Here again an arbitrary level of plant oil contamination was chosen as a basis for further preliminary work. This level is 5.0 weight percent (dotted line).

The sensitivity to contamination level is expected, although the strength of this sensitivity is a little unexpected. The result fits in direction with what would be expected for thickening due to addition polymerization at points of unsaturation (double bonds) in the plant oil. Further

confirmation of this probable reaction mode is shown in Figure 4 where viscosity rise results are shown for oleic and linoleic safflower contamination of 5 weight percent. Once again viscosity rise is greater for the higher level of unsaturation. The result for 5% sunflower oil is shown as a dotted line in Figure 4.

Effect of System Temperature

A temperature of 150°C was selected for early work for several reasons. First, it seems a good compromise between the extremes of exposure in an operating diesel engine. Crankcase oil temperatures average near 120°C, while combustion chamber surfaces exceed 200°C. As a practical matter, 150°C is a maximum experimental level due to fuming and charring problems of our reservoir bath heating oil - which itself is a specialty high stability silicone oil.

A few experiments were conducted at 120°C using several catalyst and oxygen flow levels. These results are shown in Figure 5 along with the baseline 150°C case as a dotted line. The effect of oxygen flow rate was imperceptible at 120°C, but a slight difference in the catalyst level curves can be seen. Very little viscosity rise is seen at 120°C compared with 150°C. Lower engine operating temperatures would obviously diminish the problem of crankcase oil thickening.

Effect of Sunflower Methyl Ester Contamination

Figure 6 shows the viscosity rise at baseline conditions when 5.0 weight percent sunflower methyl ester(s) is substituted for 5.0 weight percent sunflower oil. The

methyl ester(s) have similar unsaturation when compared with sunflower oil (iodine values of 139 and 140 by our testing, respectively). However, viscosity rise is much lower, showing the impact of the smaller molecular weight(s) of the ester(s) as degree of polymirization increases.

Loss of methyl ester(s) in this experiment is uncertain as our analytical capabilities expand in this project, we expect to be able to measure ester content with good precision using infrared spectroscopy.

*Preliminary Results - Alkalinity Loss

Serious alkalinity loss normally accompanies thermal deterioration of plant oil/lubrication oil mixtures. Results of preliminary evaluations of alkalinity loss presented below are again for mixtures of sunflower oil or its methyl ester(s) in API CD SAE 30 lube oil. Standard conditions of 5% contaminant, 150°C, 20 cm catalyst wire and 2000 ml/hr oxygen flow rate are used except as noted.

Mixture alkalinity is established by determination of a "total base number" or TBN. This measure is analogous to the more commonly used acid number and is determined by ASTM standard method D-2896 (potentiometric titration).

TBN Loss - Standard Conditions

Loss of total base number as a function of time for the standard experimental conditions is shown in Figure 7. TBN holds up quite well through 10-15 hours, then plummets precipitously, presumably as alkalinity maintenance additives in the lube oil are exhausted. Ultimately TBN

begins leveling off, but in a range that is unacceptably low for buffering acidic oxidation species.

Emphasis in our work will be applied to understanding and hopefully mitigating alkalinity loss in contaminated lubrication oil.

TBN Loss - Effect of Oxygen Flow

Figure 8 shows that TBN loss is little affected by increasing oxygen flow from the standard 2000 ml/hr to 4000 ml/hr. The two curves are probably not significantly different (in a technical sense) given likely experimental error in standard method ASTM D-2896.

TBN Loss - Effect of Catalyst

Figure 9 gives the effect of catalyst removal on TBN loss at standard conditions. Through the early stages of the experiment the no-catalyst cell is little different from the 20 cm catalyst standard case (dotted line). Toward the end of the experiment, the no-catalyst case seems to level off at a higher TBN. Thus the effect of eliminating catalytic metals has a small but significant effect on alkalinity maintenance.

TBN Loss - Sunflower Methyl ester Contamination

When 5.0 weight percent of sunflower methyl ester(s) is substituted for the sunflower oil contaminant, TBN falls (at otherwise standard conditions) as shown in Figure 10. Note that TBN decline is more rapid and results in leveling off at lower values than with sunflower oil (dotted line). This

may ultimately prove very important in limiting the use of ester fuels if solution of the crankcase problem(s) eludes technicians.

*Preliminary Results - Lubricity

Samples of degraded 5.0% sunflower/lube oil mixtures having a range of viscosities were sent to Phoenix Chemical Laboratories in Chicago for lubricity testing according to ASTM D-4172. The test device used is a four-ball wear tester (Figure 11) which spins a single ball bearing against three other bearings under load. Scar diameter (thickness) is measured on each ball following testing.

Figure 12 shows results of preliminary wear testing. It is seen that wear (scar diameter) is only little affected by oil mixture viscosity. Thus, oil mobility and not lubricity may be the overriding factor in the problem of crankcase oil viscosity build-up.

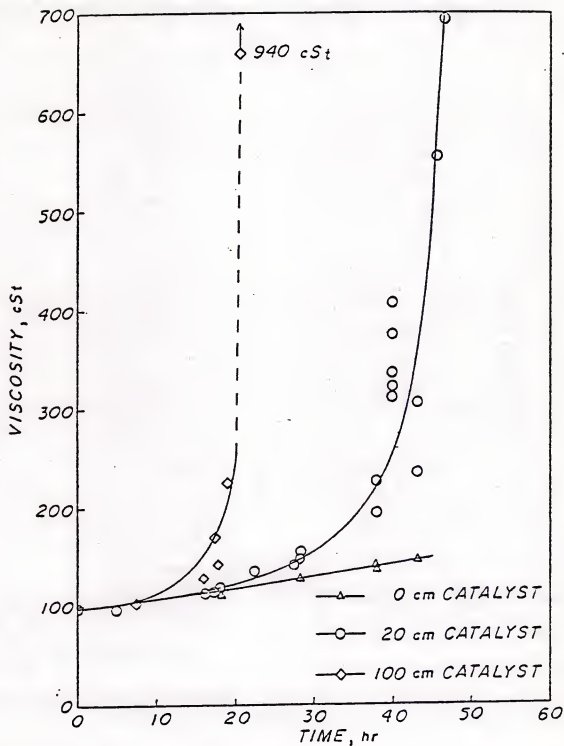


Figure 1. Viscosity vs. time for 0, 20, and 100 cm copper-iron catalyst and 2000 ml/hr oxygen.

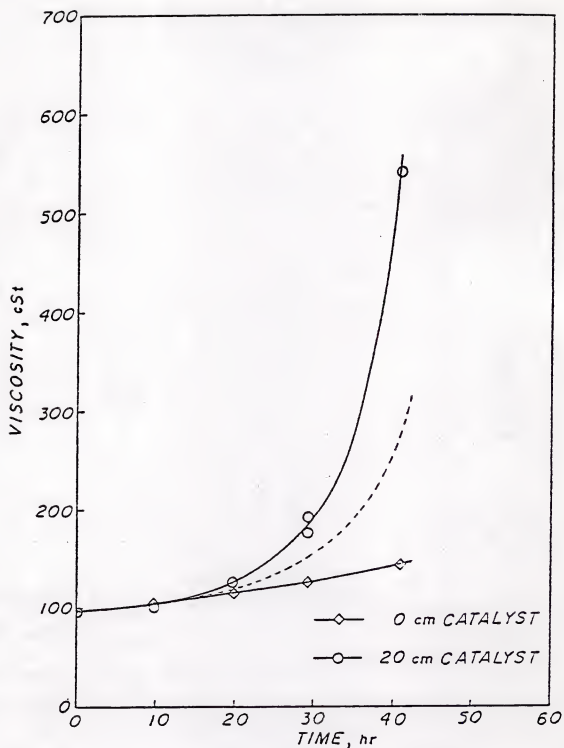


Figure 2. Viscosity vs. time for 0 and 20 cm copper-iron catalyst and 4000 ml/hr oxygen.

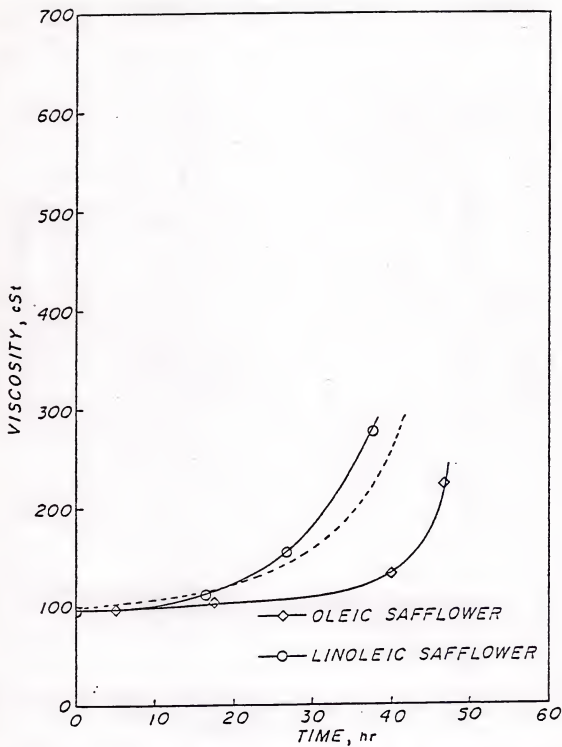


Figure 4. Viscosity vs. time for 5 wt. % linoleic and oleic safflower oil, with 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

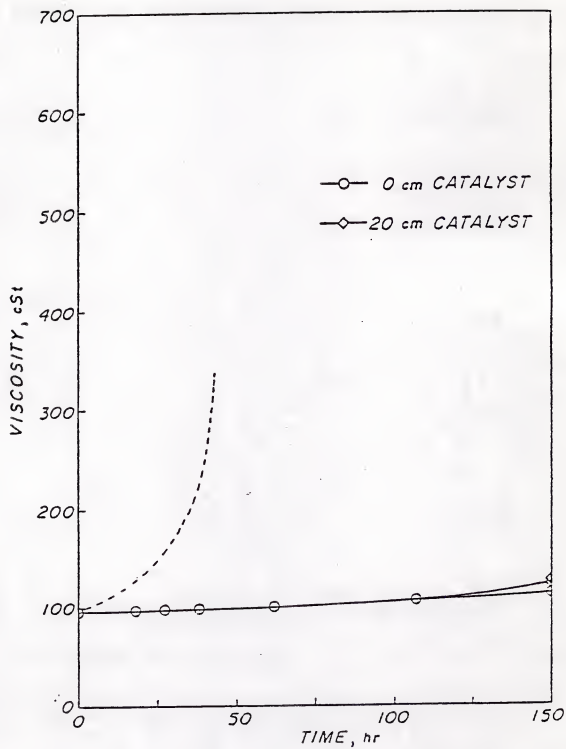


Figure 5. Viscosity vs. time for 120 C. with 0 and 20 cm copper-iron catalyst, and 2000 and 4000 ml/hr oxygen.

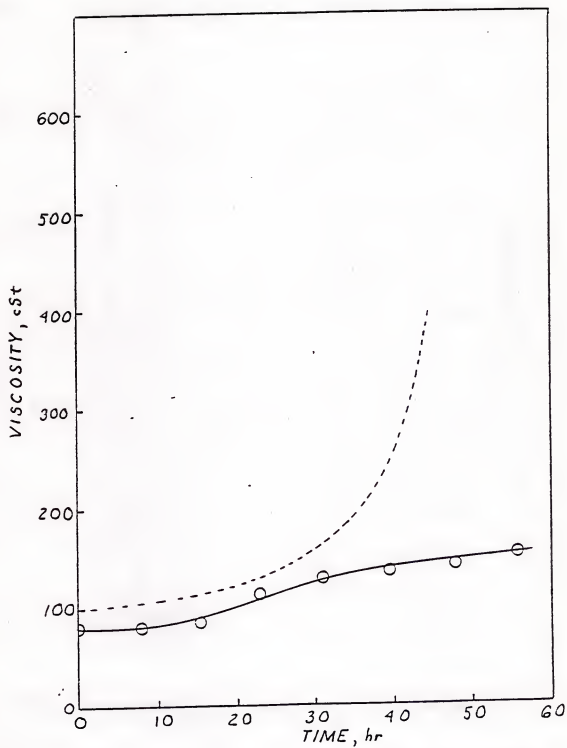


Figure 6. Viscosity vs. time for 5.0% sunflower methyl ester(s) at standard conditions.

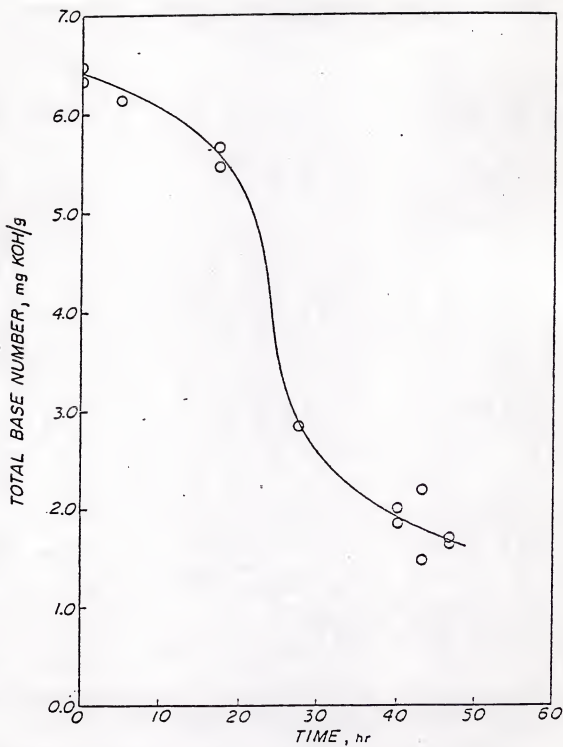


Figure 7. TBN vs. time for 20 cm copper-iron catalyst and 2000 ml/hr oxygen.

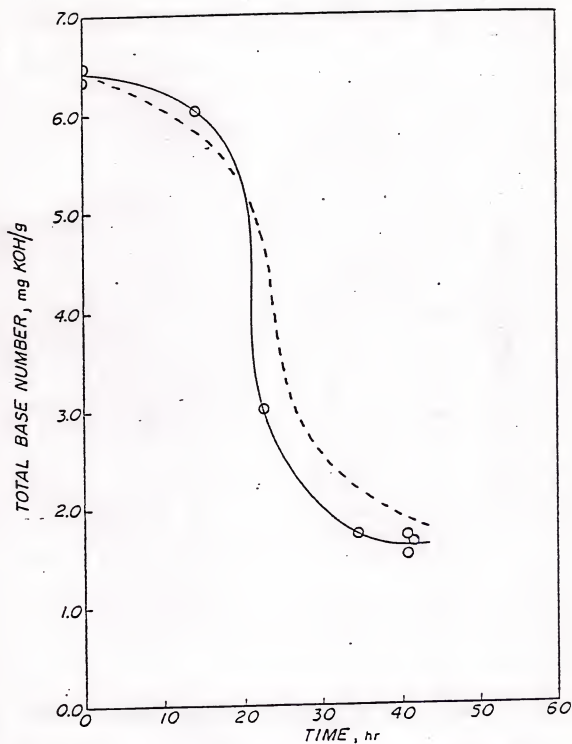


Figure 8. TBN vs. time for 20 cm copper-iron catalyst and 4000 ml/hr oxygen.

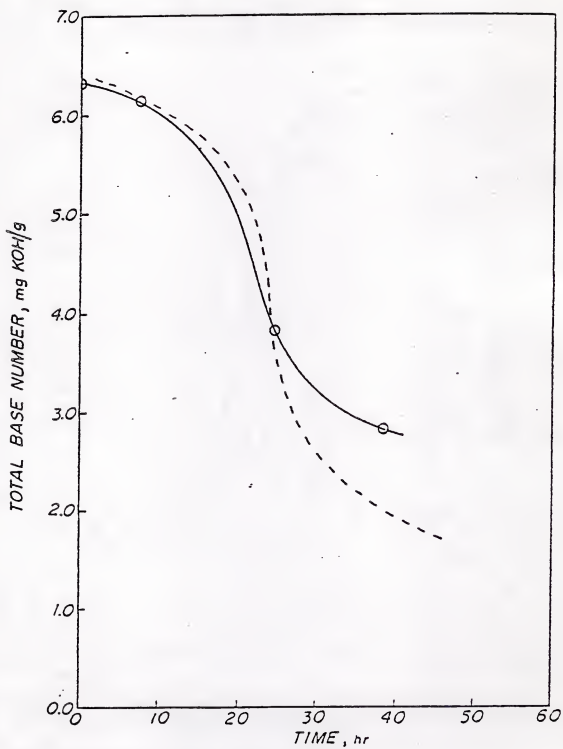


Figure 9. TBN vs. time for no catalyst and 2000 ml/hr oxygen.

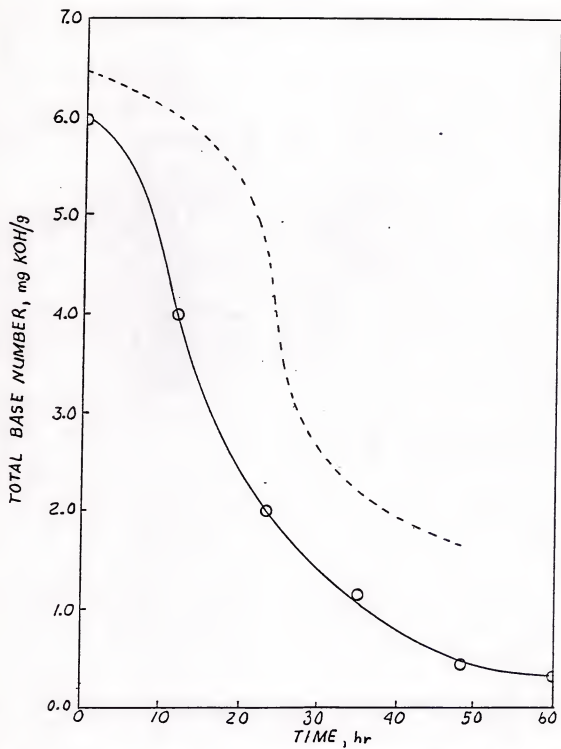


Figure 10. TBN vs. time for 5.0% sunflower methyl ester(s) at standard conditions.

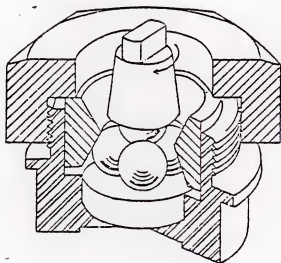


Figure 11. Detail of four-ball wear tester.

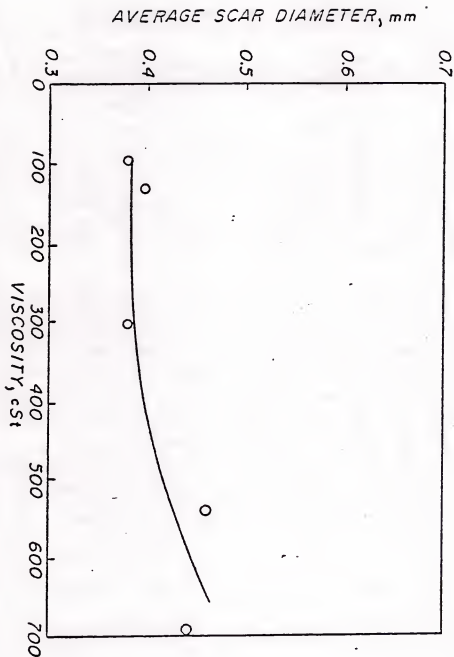


Figure 12. Average scar diameter vs. viscosity for 5 wt. % sunflower oil, with 20 cm copper-iron catalyst.

"CONTAMINATION OF DIESEL ENGINE LUBRICATION OIL
BY PLANT OIL DERIVATIVE FUELS"

Milestone Report #2

Comparison of Fuel Candidates

In Milestone Report #1 the impacts of sunflower oil contamination in diesel lube oil was reported. A wide range of experimental conditions was investigated to determine the extent of oil mixture deterioration. Oil mixture deterioration was quantified by measuring increase in kinematic viscosity and simultaneous loss of alkalinity (total base number). A standard set of experimental conditions was fixed as a result of this initial work. The methyl ester(s) of sunflower oil was evaluated as a contaminant at the standard conditions with results also presented in Milestone Report #1.

This Milestone Report #2 evaluates a group of additional Montana-specific plant oils as diesel fuel candidates. Evaluation is again based upon viscosity rise and alkalinity loss in mixtures with diesel lubrication oil at standard experimental conditions. The lubrication oil used is API CD SAE 30. This oil has been used as a basis over two years of study and is the logical choice for comparing plant oil fuel candidates. Standard conditions include: 5.0% by weight plant oil concentration, 150°C bath temperature, 2000 ml/min oxygen percolation rate, and exposure to metallic copper catalyst.

Plant oil fuel candidates studied were: rapeseed oil, safflower oil, the methyl ester(s) of rapeseed oil, and the ethyl ester(s) of sunflower oil. Included for comparison are the earlier results with sunflower oil and its methyl ester(s), shown as dashed lines on the following figures for viscosity rise and total base number decline.

*Plant Oils

Figure I gives viscosity rise results for the three plant oils. As noted, the sunflower oil result reported earlier is shown as the dashed line. The three curves show the same exponential shape and have similar magnitudes, well within the expected error of the technique. Thus, on the basis of viscosity rise, all three oils pose roughly the same problem for an engine lubrication system.

Loss of alkalinity results for the three plant oils in the 30-weight lube oil are given in Figure II. The Safflower and rapeseed oils show very similar rates of alkalinity loss. However, sunflower oil yields a generally slower loss of alkalinity with a distinct S-curve profile. A change in experimental technique probably explains the difference in the curves of Figure II. Between the TBN measurements for the sunflower oil system and those for the other two oils, the type of potentiometric titrimer used in the analysis was switched due to a malfunction of the former unit. At this time it is assumed that varying titrimer sensitivity accounts for the bulk of the variation shown in Figure II.

On the basis of Figures I and II, the three plant oils show overall comparable performance as diesel fuel candidates. Each oil (at 5.0% in lube oil) poses serious problems of thickening and acidification which must be solved before any has significant potential as an alternative diesel fuel.

Table I gives iodine value measurements for the three plant oils. Iodine values are proportional to unsaturation ("double bonds"), and generally one would expect oxidative reactivity to be proportional to iodine value. However, the results shown in Figures I and II are not in line with iodine values. Inherent small errors in viscosity and TBN measurements as well as in the iodine value testing could easily hide the expected correlations.

Table I

<u>Fuel</u>	<u>Iodine Value</u>
Sunflower Oil	138
Safflower Oil	130
Rapeseed Oil	120

*Esters of Plant Oils

Figure III gives viscosity rise results for the methyl ester(s) of rapeseed oil and the ethyl ester(s) of sunflower oil. For comparison the earlier result for the methyl ester(s) of sunflower oil is included as a dashed line.

There are several striking features in Figure III. First, it is seen that the rates of viscosity increase are much lower for the esters as contaminants in the lube oil at 5.0% than for the parent oils. As was hypothesized earlier for the methyl sunflower result, it seems probable that the smaller molecular size of the esters explains most of the viscosity rise reduction. All curves seem to level off at longer exposure times, quite unlike the continuous exponential rise exhibited by the parent oils. Evaporative loss of the esters may explain some of the leveling off, but sludge formation at longer exposure times may also be involved. All ester trials gave a gel-like precipitate at 30-40 hours of exposure. Insolubility of higher molecular weight polymers may well be causing the observed leveling off of viscosity over time with the esters. Thus, while these materials give much reduced apparent viscosities as contaminants in lube oil, sludge formation may restrict their use as diesel fuel. It is interesting to note that sludge formation with the ester fuel candidates occurs at about the same time as viscosities for the parent plant oil systems accelerate rapidly.

Figure IV gives alkalinity results for the three ester fuel candidates. Again, the dashed line is methyl sunflower. All three esters show roughly the same rate of alkalinity loss. The initial TBN value for the ethyl sunflower in lube oil is distinctly lower than the others, but the rate of acidification is similar. The lower initial value is probably a result of ester sample age - this sample was obtained from John Deere Corporation and was about two years old.

Table II gives iodine values for the two methyl esters. No value is presented for the sunflower ethyl ester(s) as only enough sample (25 ml) was available for exposure testing. Again, with the esters, Figures III and IV show little correlation with unsaturation. Total base numbers are in accord with the unsaturation levels, but viscosity rise shows no dependence on iodine value. Any dependence may be lost in the scatter of the data.

Table II

<u>Fuel</u>	<u>Iodine Value</u>
Methyl Sunflower	140
Methyl Rapeseed	115

*Summary Evaluation

All five fuel candidates pose serious problems for the lubrication system of a diesel engine. The plant oil esters show less thickening than the parent oils, but a serious sludge problem exists. All materials cause sharp losses of alkalinity well short of a typical lube oil change cycle of 80-100 hours. Solutions to both problems (three, counting sludge) must be found before any of these materials become realistic fuel candidates.

Other Milestone Highlights

*Mechanism - Additive Chemistry

Trials with basestock oils for both 30-weight truck/tractor and 45-weight locomotive lubricants contaminated with sunflower oil have exhibited extreme degradation at short exposure times at standard conditions. Additions of single additives of known chemical composition are now being tested. One additive, zinc diamyldithiocarbamate, shows significant promise for reducing thickening and sludge formation. Work with this additive injected into basestock and commercial (containing proprietary additive "packages") lube oils is continuing and will be reported in detail in Milestone Report #3.

* Catalysis Mechanism

Progress is being made in understanding the role of copper as a polymerization and oxidation catalyst. There are strong indications that soluble forms of copper are very important in the reaction mechanisms. Metallic copper can be removed from test cells midway through an exposure trial, and the viscosity rise continues as if the copper were still present. Metallic copper can also be replaced with an organic copper complex, cupric acetylacetonate, presumed to be soluble in plant oil/lube oil mixtures, and again rapid polymerization is observed. These results hold special promise, as it is inherently easier to "tie up" or render inactive soluble forms of catalysts. Details of this work will also be provided in Milestone Report #3.

↑ 1290 Cs
△

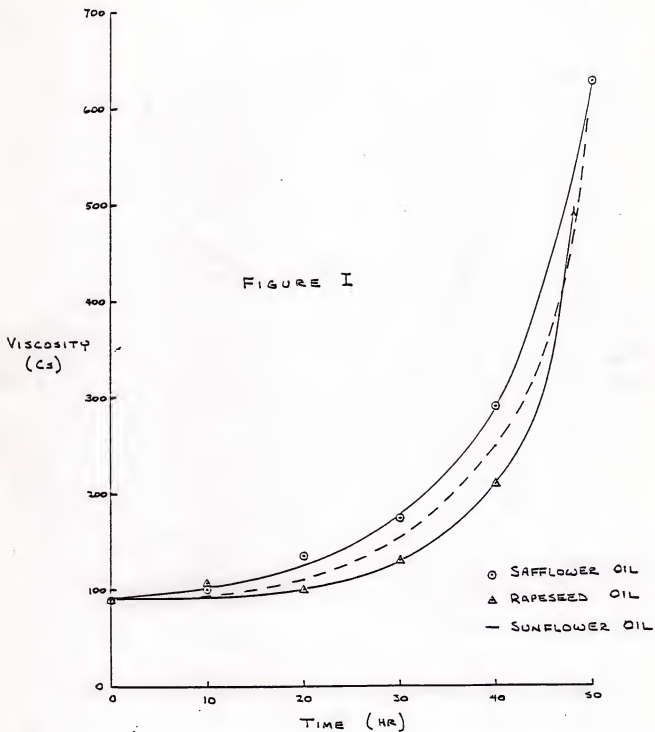
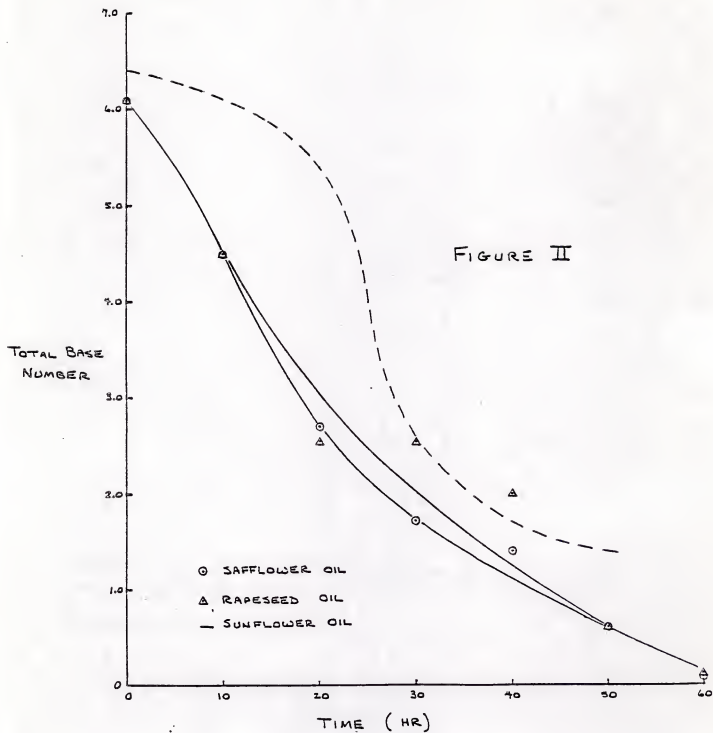
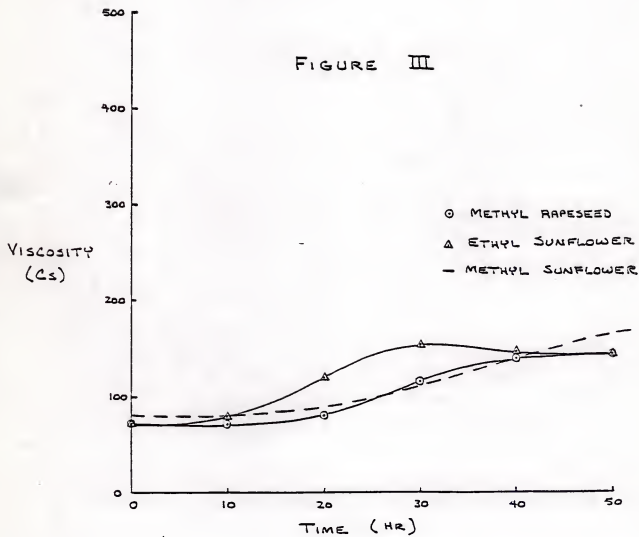
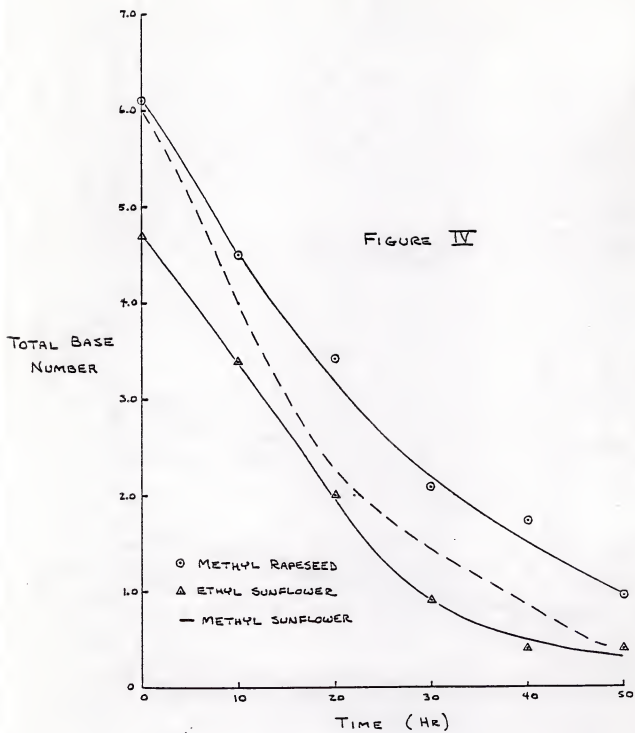


FIGURE II







CONTAMINATION OF DIESEL ENGINE LUBRICATION OIL
BY PLANT OIL DERIVATIVE FUELS

Milestone Report #3

Milestone Reports #1 and #2 presented the polymerization behavior of various plant oil derivatives as contaminants in lubrication oil at exposure conditions simulating a diesel engine crankcase. This report summarizes results of an investigation seeking the fundamental mechanism(s) of the oil mixture polymerization. Both free radical and ionic polymerization mechanisms were studied along with the role of copper as a polymerization catalyst.

Hydrocarbon basestock for SAE 30 lube oil was initially selected as the substrate lubrication fluid for this study with refined sunflower oil (iodine value 138) as the test contaminant. Sunflower oil was selected based upon a wide breadth of experience with its use in this laboratory, and the fact that other plant oils of significance in Montana show overall similar polymerization behavior. No plant oil derivative esters were used since these contaminants produced excessive sludge of an unknown chemical nature in work reported in Milestone #2.

Initial experiments with the SAE 30 hydrocarbon basestock yielded severe sludge formation in the early stages of all experiments

with sunflower oil contamination. This rapid degradation forced the research to use commercial lube oil (with additives) for the mechanism study. The oil selected, Amoco Super HD II API CD SAE 30, contains an additive recipe of proprietary chemistry, unknown to us. However, we have considerable experience with this oil, and the mechanism study yielded a seemingly clear cut result. Continued work will confirm results reported here with 45 weight locomotive lube oil and hydrocarbon basestock(s) as we gain facility with the latter. Results with these alternate lube oils will be presented in Milestone #4.

*Ionic Polymerization Study

The presence of acids, and hence H^+ ions, can under some conditions catalyze addition polymerization. The first phase of the present mechanism study looked for evidence that ionic catalysis is a factor in the polymerization of plant oil contaminants in lubrication oil. Alkalinity loss measurements (Milestone #2) indicated acid generation during standard exposure testing of contaminated lube oil, leading to speculation that ionic (acid) catalysis plays a role in plant oil polymerization.

Initial trials to test for ionic catalysis involved adding phosphoric acid to a level of 3.0% at the beginning of a standard 5.0% sunflower/SAE 30 CD trial. Immediate total base number (TBN) values were erratic, but at twelve hours the TBN value was 0.18 mg KOH/g,

indicating little alkaline reserve. The viscosity rise behavior for this phosphoric acid trial is given in Figure 1. Also given in Figure 1 (as a dashed line) is the standard 5.0% sunflower/lube oil response.

Figure 1 shows that free mineral acid does not accelerate plant oil polymerization over 40 hours of exposure. The two curves are very nearly the same, with the standard trial actually polymerizing somewhat faster. Thus, there is no evidence of ionic catalysis in this trial.

Since ionic catalysis might operate with only small quantities of free acids and be insensitive to excess amounts, it was decided to confirm the indication of Figure 1 in a reverse manner; i.e., maintain TBN at a high value and test for reduced polymerization. To accomplish this, an alkalinity maintenance additive, Amoco 9231, was utilized. This compound, an overbased calcium phenate, was added periodically to a standard 5.0% sunflower/lube oil trial to keep alkaline reserve up and simultaneously measure extent of polymerization.

Results of the alkalinity maintenance trial with Amoco 9231 are given in Figure 2. Points in time where TBN ascends vertically correspond to additions of the additive. Normally, (without the additive) TBN falls to approximately 2.0 at 40 hours exposure. Here TBN averages near 6.0 for the entire exposure. A comparison of viscosity rise in the present case with the standard response (no

additive, dashed line) again fails to show any ionic catalysis impact. Clearly, free acid content is reduced, but polymerization proceeds at a normal pace.

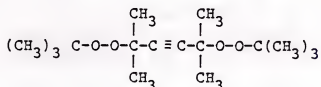
The results of Figures 1 and 2 rather conclusively show that ionic catalysis plays at most a minor role in polymerization of plant oil contaminants in the lube oil. It is possible that unknown additives in the lube oil mask the ionic catalysis impact, but this seems unlikely. This potential complication will be tested later in the work as we learn to utilize hydrocarbon basestock lube oil as a substrate.

*Free Radical Polymerization Study

Addition polymerization of unsaturated compounds, especially polyunsaturated compounds, can proceed by a free radical mechanism. Mechanism details can be quite complex as summarized by Wexler (1), but all such mechanism pathways involve oxidation or additive chemicals that directly decompose to yield free radical intermediates that then initiate polymer chain reaction.

The standard case exposure of contaminated lube oil used in this research (Milestone #1) involves percolation of oxygen through test samples at 150°C. To test whether a free radical mechanism is involved in the polymerization, continuous oxygen bubbling was

eliminated from the routine and replaced by periodic additions of Lupersol 130, a free radical generator. Lupersol 130, a Lucidol Pennwalt organic peroxide product, has the structure



This compound is known to cleave between oxygen atoms to yield free radicals with an estimated half life of 57 minutes at 150°C.

Figure 3 gives results for two trials where Lupersol 130 was added every 2.5 hours to a 5.0% sunflower/lube oil system. Addition levels were 0.5% and 0.1%. Also shown in Figure 3 as a dashed line is the standard case with oxygen percolation. It is seen that the magnitude and general shape of the standard viscosity rise curve can be reproduced with the peroxide additive and no oxygen. This is strong evidence that the standard case polymerization (viscosity rise) results from an oxygen-induced free radical mechanism.

Continued research will now focus upon antioxidant additives that inhibit free radical pathways to polymerization. These additives may decompose intermediate hydroperoxides, stabilize free radicals or consume free radicals, or even have combination effects.

One free radical inhibition compound, zinc diamyldithiocarbamate, shows promise for the lube oil contamination problem. This

material may decompose hydroperoxides formed as a double bond is oxidized before the hydroperoxide can cleave into a pair of free radicals. Preliminary experiments with SAE 30 basestock and 5.0% sunflower oil yield little polymerization or sludge. This work will be reported in detail in Milestone #4.

*Copper Catalysis Work

The nature of copper as a polymerization catalyst at conditions of this study is complex. As reported in Milestone #1 polished metallic copper foil is a strong polymerization catalyst, and the rate of polymerization is a moderate function of the amount of foil immersed in the sample mixture. As an experiment progresses the foil develops a reddish coating, probably oxides. However, trials using only copper oxides (no metal foil) fail to show any appreciable catalytic activity.

In some trials using copper foil catalyst, a black sludge forms, coating the metal surface. This was especially true in early runs using hydrocarbon lube oil basestock with no additives. Such coatings raised the question of whether copper surface or dissolved copper species contribute the bulk of the observed catalysis. To address this issue SAE 30 API CD lube oil was exposed to standard conditions for 48 hours in two trial cells with no plant oil present. In one trial oxygen at 2000 ml/hr was used and in the other nitrogen at the

same volumetric flow rate. At 48 hours the copper foil was removed from the two cells and 5.0% sunflower oil was added to each. Oxygen flow was substituted for the nitrogen in one cell. Both flasks were then subjected to continued exposure with standard conditions except for the absence of copper foil.

Results for these two trials along with the standard case for 5.0% sunflower oil (dashed line) are given in Figure 4. The time origin for the two novel trials is the 48 hour mark. Also shown in Figure 4 is a dotted curve for sunflower oil contamination where no copper was used. Note here that the standard case curve shows more rapid polymerization than depicted in earlier figures. A new lot of SAE 30 lube oil was used for all trials shown in Figure 4, and in this mixture the sunflower oil consistently polymerized as shown. Presumably, a modified additive recipe is responsible for this behavior.

From the point of sunflower oil addition, the two trial cells (with copper foil removed at 48 hours) polymerize in a similar manner to the standard case. Both cells polymerize much more rapidly than the case where no copper was ever present. The results of Figure 4 strongly indicate that dissolved copper may dominate the catalysis of triglyceride polymerization. Further, it appears that the long induction period observed in the standard case sunflower experiment may be partially determined by the rate of copper dissolution. The difference between the two trial cells after plant oil addition (48

hours) is uncertain, but oxygen may gradually convert dissolved copper species to inactive oxides, causing the observed reduced polymerization. Further work will focus upon this difference.

To further test the concept of dissolved copper catalysis, cupric acetylacetonate (CAA) was investigated as a homogeneous catalyst. This compound appeared to dissolve in sunflower/lube oil mixtures at room temperature. Figure 5 presents results for three sunflower oil trials using cupric acetylacetonate at initial concentrations of 1 ppm, 5 ppm and 10 ppm based upon copper (weight). All conditions were standard other than the form of copper used. It is again seen that the standard copper foil case (dashed line) can be approximated with a substitute homogeneous copper catalyst.

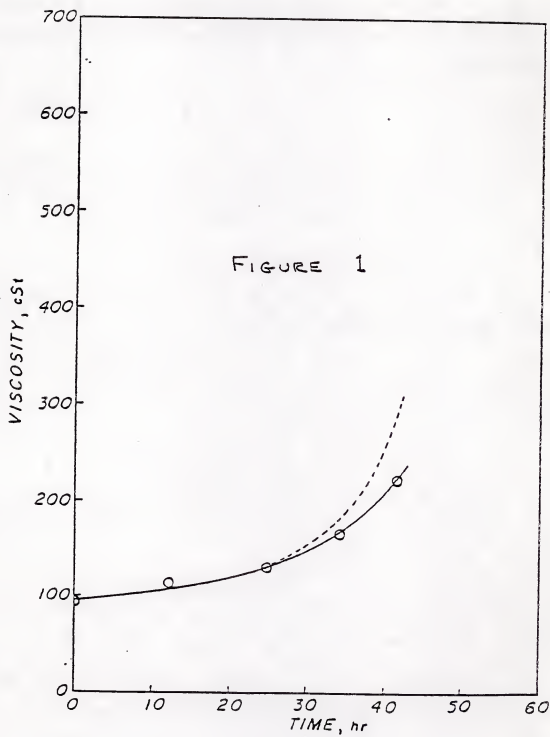
Another trial using no copper (any form), no oxygen, and periodic additions of 0.5% Lupersol 130 peroxide (as reported above) essentially reproduced the earlier 0.5% peroxide curve of viscosity versus time achieved with copper foil. This result indicates that copper catalyzes the free radical formation stage of polymerization (initiation), but does not influence the propagation of the chain reaction.

*Other Milestone Highlights

Research is proceeding to mitigate the polymerization effects of free radical oxidation and copper catalysis. Zinc diamyldithio-carbam

ate is being actively studied as an antioxidant with hydrocarbon basestock and commercial lube oils. A research plan is also being initiated to develop chelating or sequestering systems/agents to inactivate soluble copper catalyst species. Details of this work will be presented in Milestone #4.

1. Wexler, H., Chem. Rev. 64:6 (1964).



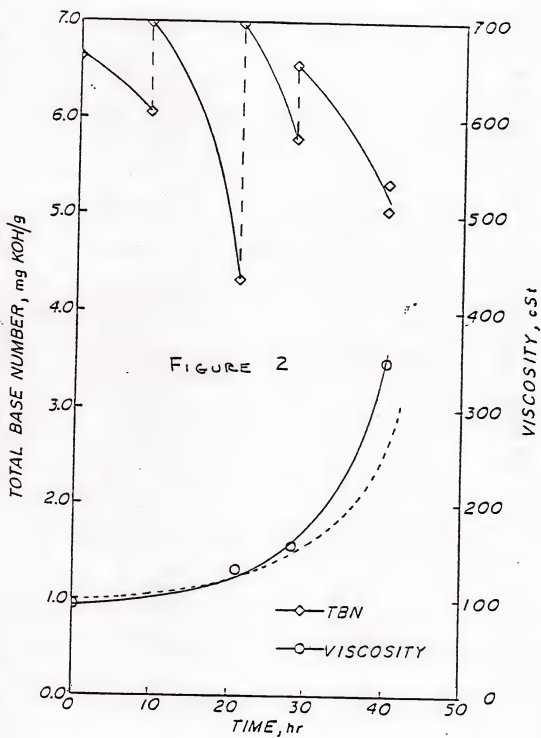


FIGURE 3

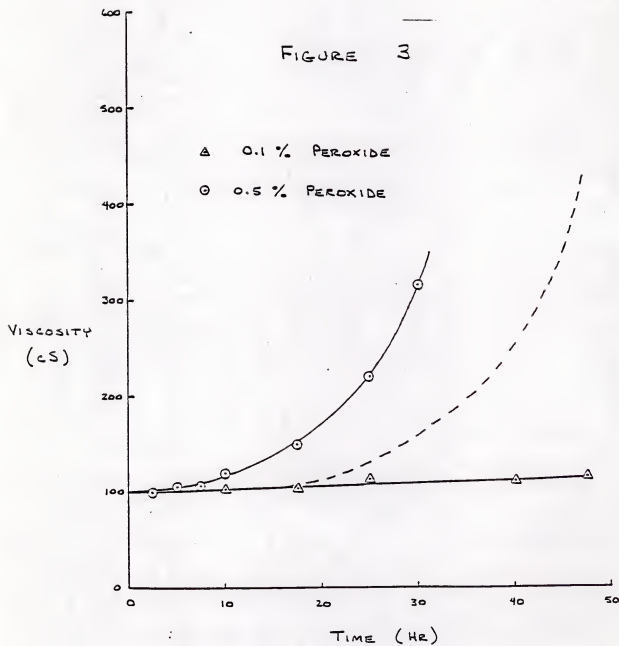
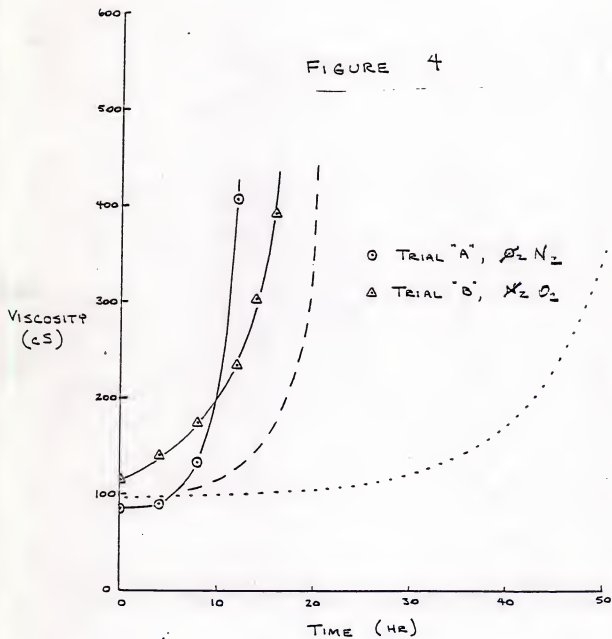
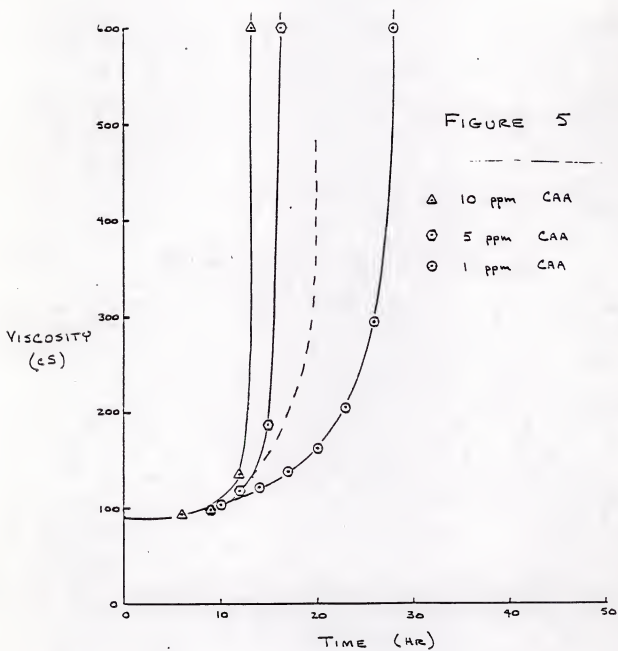


FIGURE 4





CONTAMINATION OF DIESEL ENGINE LUBRICATION
OIL BY PLANT OIL DERIVATIVE FUELS

MILESTONE REPORT #4

Milestone Report #3 gave strong evidence that the polymerization of sunflower oil as a contaminant in diesel lubrication oil proceeds by a free radical mechanism. A known free radical generator (Lupersol 130, a Lucidol Pennwalt organic peroxide) produced sunflower oil polymerization that matched standard experiments in the absence of otherwise required oxygen reactant. A number of other experiments reported in Milestone #3 altered oil mixture acidity/basicity with acid or alkaline agents without affecting polymerization of sunflower oil contaminant. This seemingly rules out ionic catalysis as a dominant polymerization mechanism.

Work reported in this milestone report focused upon inhibition of free radical catalysis and continued research into the role of metallic catalyst(s) present in used lube oil as wear metals. Two lubrication oils were used in the work: API CD SAE 30 commercial oil (Amoco Super HD II) and the additive-free hydrocarbon basestock of this oil. Only sunflower oil was tested as a fuel contaminant. As reported in Milestone #2 other Montana-specific plant oils produced similar polymerization results as with sunflower oil, and plant oil ester derivatives gave weaker viscosity responses.

Free Radical Inhibition

Prevailing theories for free radical addition polymerization (1,2) propose a sequence of mechanism steps that involve unsaturated monomers, oxygen, heat and sometimes catalysts, if present. Additives that might inhibit the polymerization and hence block the unwanted build-up of viscosity of lube oil/fuel oil mixtures can achieve the inhibition effect by interrupting the mechanism at any step.

The first step in the mechanism of free radical addition polymerization involves oxygen attack at points of unsaturation (double bonds) in the triglyceride oil. The initial result of this oxidation is creation of unstable hydroperoxides. The hydroperoxides spontaneously decompose to yield free radical species which then attack points of unsaturation in other plant oil molecules and thus propagate the addition chain reaction

A widely used commercial antioxidant, Lubrizol 1395, was tested first as a polymerization inhibitor. This product is zinc dialkyl dithiophosphate (ZDTP) and is speculated to inhibit oxidation of motor oils by converting hydroperoxides to non-radical products. This ZDTP was added at 1.0% to a mixture of 95% basestock lube oil/5% sunflower oil. The use of hydrocarbon basestock as the lube oil substrate is practically required if a complete understanding of the system chemistry is sought. This is due to the unknown chemical nature of the additive "recipe" in commercial oil. Standard conditions of 150°C, oxygen percolation and presence of copper foil catalyst were employed. The result of this trial is shown in Figure 1 along with a control experiment (dotted line) where no ZDTP was used.

Figure 1 shows that there was no appreciable rise of viscosity in either case, with or without ZDTP. However, in each case a great deal (perhaps 10% by volume) of insoluble gel or "sludge" was found on the walls and other surfaces of the exposure vessel. This sludge appears to be polymerized plant oil swollen by lubrication oil but not soluble in it. The difference between this sludge formation in basestock oil and the viscosity build-up in commercial SAE 30 lube oil may be due to dispersing agent(s) present in the commercial oils. If the dispersing agent(s) is capable of dispersing or even solubilizing polymers as they form in the oil mixture, these polymers would be primarily observed as contributing to a viscosity build-up and not as creation of a separate phase. Conversely, in the basestock case no dispersant is present and insoluble polymer would form as a separate phase attached to reaction cell surfaces.

In either case, the rapid formation of sludge when sunflower oil is present in basestock or the large viscosity build-up when it is present in commercial lube oil leads to a major obstacle for the use of plant oil fuels. Neither lube oil stock shows significant degradation, of either type, when sunflower oil is not present as a contaminant.

Another antioxidant, Vanlube AZ, was next tested as a polymerization inhibitor. This compound is zinc diamyl dithiocarbamate (ZDTC) and is also speculated to produce non-radical species from unstable hydroperoxide intermediates. The manufacturer of Vanlube AZ, Vanderbilt Corporation, also suggests that the ZDTC can inhibit polymerization by terminating the chain reaction through destruction

of free radicals. Vanderbilt also suggests that ZDTC may deactivate metallic polymerization catalysts.

Figure 2 gives the viscosity rise results for the use of ZDTC at 0.5% and 1.0% in the 95% basestock/5% sunflower oil mixture. Again no appreciable viscosity rise is observed, but in these cases no sludge was formed until nearly forty hours exposure, and beyond this point sludge formation was only slight. The standard conditions of 150°C, oxygen percolation and copper foil catalysts were employed in the trials of Figure 2.

Clearly, the addition of ZDTC yields a breakthrough in inhibiting the degradation of sunflower oil in a lube oil mixture. In all other trials with commercial or basestock lube oil at standard conditions, sunflower oil degradation was observed as either rapid viscosity rise or excessive sludge formation. The zinc diamyl dithiocarbamate seems to be sharply inhibiting the polymerization(s) leading to these degradation effects.

Next ZDTC was tested at 1.0% and standard conditions in a 95% basestock/5% sunflower mixture except oxygen was replaced with inert nitrogen flow and Lupersol 130, the free radical generator, was periodically added as reported in Milestone #3. The structure of Lupersol 130 is



This compound spontaneously decomposes to free radicals at the peroxy links. If ZDTC works by scavenging free radicals, it should slow the known polymerization rate with Lupersol 130.

Figure 3 shows viscosity rise data for the Lupersol 130 experiment, with and without the use of 1.0% ZDTC. The results are similar, but the trial with ZDTC shows a somewhat reduced viscosity rise. The ZDTC may be inhibiting polymerization by partially blocking the decay of Lupersol 130 into free radicals or perhaps by consuming some free radicals as they are formed. Whatever the effect of ZDTC, it is not pronounced when tested in conjunction with a non-oxidative free radical generator.

Of significant interest in Figure 3 is the fact that sludge was essentially absent in both trials while the viscosity increases are greater than any trial wherein significant sludge was formed. Why sludge does not form in these Lupersol 130 trials is not known and is a subject of continuing work in this project.

Zinc diamyl dithiocarbamate was next tested at 0.5% and 1.0% in a standard exposure trial using commercial lube oil in place of the basestock. Oxygen and copper catalyst were used as normal. Results of these trials are shown in Figure 4. The trials with differing ZDTC levels are practically identical, but both show a distinct inhibition of viscosity rise compared with a control experiment containing no ZDTC. Although ZDTC forestalls the viscosity rise for 10-12 hours, it is not nearly as effective in inhibiting viscosity rise as it is in minimizing sludge formation in hydrocarbon basestock experiments. Perhaps some unknown additive in the commercial lube oil is deactivating the ZDTC or is promoting polymerization by a mechanism(s) not fully inhibited by ZDTC. This issue is also a topic of continued research.

Finally, two other proposed addition polymerization inhibitors were tested in standard trials using a 95% hydrocarbon basestock/5% sunflower mixture. These compounds were Vanlube 81 (Vanderbilt) and Ethanox 702 (Ethyl Corporation) and each is supposedly active in consuming free radicals and thus inhibiting the propagation step of polymerization. Vanlube 81 is a dioctyl diphenylamine and Ethanox 702 is 4,4' methylene bis (2,6 ditert butyl phenol). Neither of these additives showed any inhibitory strength, each essentially showing the inactive behavior of ZDTP in an earlier trial.

Catalysis Studies

The role of dissolved copper as an addition polymerization catalyst for the 95% commercial SAE 30/5% sunflower oil mixture at standard conditions was presented in Milestone #3. Dissolved copper can be produced in the system by prolonged exposure of metallic copper foil or by addition of the soluble copper complex, cupric acetyl acetonate (CAA). In either case a rapid viscosity rise is found with the commercial lube oil substrate.

When hydrocarbon basestock oil was substituted for the commercial oil using 5 ppm CAA in place of the copper foil, viscosity rise was only slight, but large sludge deposits were found at less than 10 hours exposure. This is practically identical behavior to the basestock experiment using copper foil shown as control in Figure 1. Just as with sunflower in commercial oil, 5 ppm CAA and metallic copper foil yield very similar results in the basestock/sunflower oil mixture.

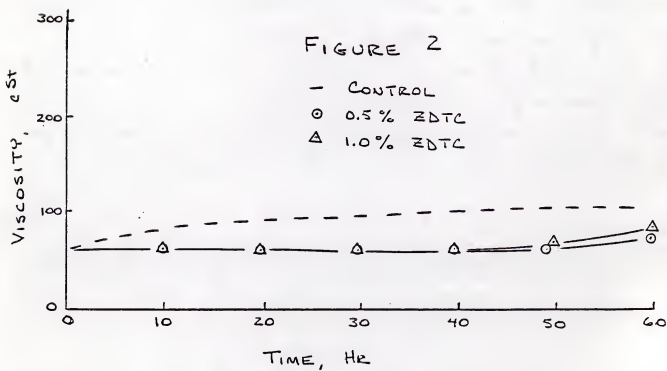
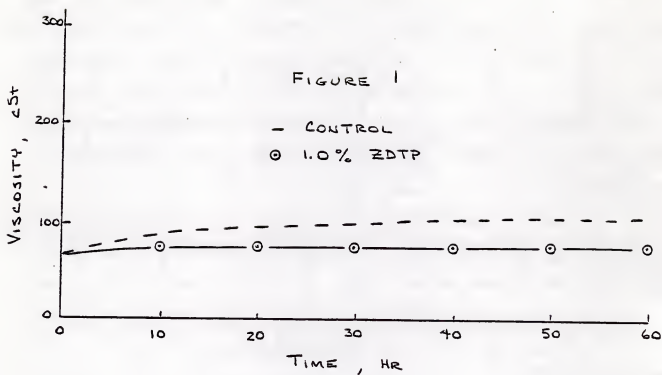
Next ZDTC at 1.0% was used in the 95% basestock/5% sunflower mixture with 5 ppm CAA replacing copper foil catalyst. The viscosity rise was practically nil, and just as with copper foil, sludge formation was minimal out to 50 hours exposure. This result indicates that ZDTC does not work in the foil experiments by deactivating the metal surface, and further indicates that the primary role of ZDTC is inhibition of free radical initiation.

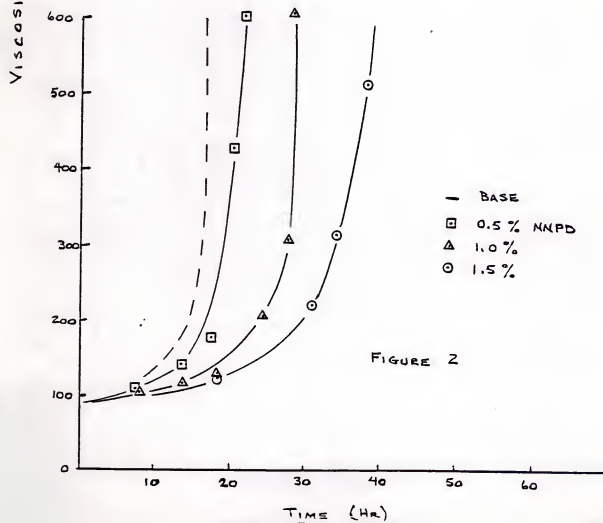
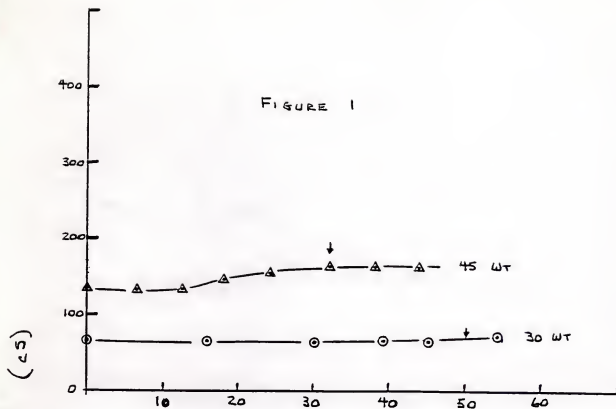
Preliminary trials have scouted the catalytic activities of lead and aluminum as metal foils. Both are commonly observed as wear metals in used diesel motor oils. In these initial experiments neither metal shows any catalytic activity for addition polymerization of sunflower oil. This work is being conducted in commercial oil to avoid the sludge problem and utilize the more "quantifiable" viscosity measure. Further trials are planned with soluble complexes, especially for lead. However, at least at this time, copper seems to be the only common engine wear metal that catalyses the plant oil polymerization. Iron was tested at the beginning of this study and found to have no catalytic effect.

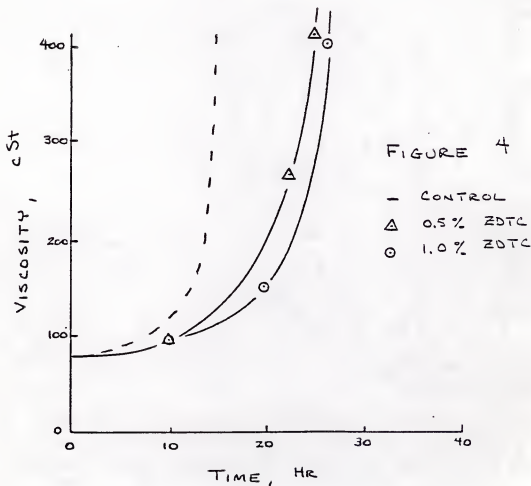
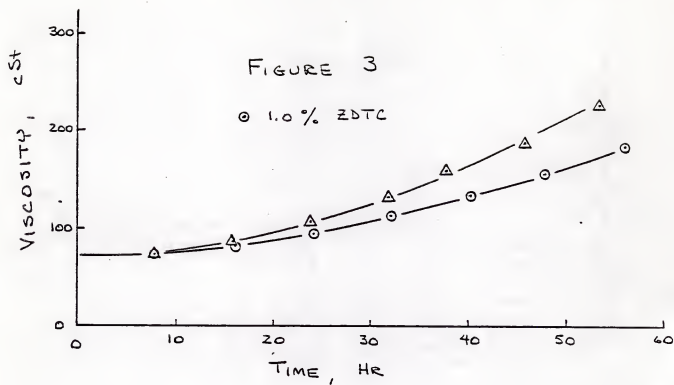
Chelating agents that may inactivate soluble forms of copper are being sought in the technical literature. A key issue is identification of agents that are thermally stable over prolonged intervals at 150°C. Results will be presented in Milestone #5.

References

1. Formo, M.W., Bailey's Industrial Oil and Fat Products, 4th Ed., Vol. 1, Swern, D., Ed., John Wiley & Sons, New York (1979).
2. Wexler, H., Chem. Reviews 64(6):591 (1964).







CONTAMINATION OF DIESEL ENGINE LUBRICATION
OIL BY PLANT OIL DERIVATIVE FUELS

MILESTONE REPORT #5

Milestone Report #4 confirmed that the polymerization of 5% sunflower oil fuel contamination in diesel lubrication oil proceeds by a free radical mechanism. A zinc-based antioxidant, zinc diamyl dithiocarbamate (ZDTC), was found to strongly inhibit polymerization of the triglycerides in SAE 30 hydrocarbon basestock, but caused only a weak inhibition of polymerization in SAE 30 commercial lube oil. The latter result is apparently due to an interaction between the antioxidant and the lube oil additive package.

In the present milestone report the use of ZDTC is extended to 45 weight locomotive lube basestock, testing for the formation of insoluble gel. In addition, further evaluation of gel produced in SAE 30 basestock experiments is reported. Finally, results of further investigation of metal catalysis of polymerization are presented, including work with a promising copper deactivator.

Polymerization Inhibition

Zinc diamyl dithiocarbamate (ZDTC) was tested at 1.0% at standard exposure conditions - 5.0% sunflower, 150°C, copper foil catalyst, oxygen percolation - in 45 weight diesel locomotive basestock oil. This basestock oil is a hydrocarbon mixture with no stabilizing additives. Viscosity rise results for this trial are given in Figure 1 along with the corresponding results for 1.0% ZDTC with SAE 30 basestock and 5.0% sunflower.

Figure 1 shows that viscosity rise is not significant for the locomotive basestock trial - an expected result since both basestocks are chemically similar hydrocarbons. Of greater interest is the impact of ZDTC on insoluble gel (polymer) production, as yet an unpredictable aspect of any basestock trial. Arrows mark the onset points of discernible amounts of insoluble gel in the two experiments presented in Figure 1. Gel is present at 32 hours in the locomotive trial, but its onset is not until 50 hours in the SAE 30 case. The precision of this difference is uncertain, but the difference may be important if oil drain-out cycles in locomotives fall within the general range of these trials.

Ongoing research with ZDTC in locomotive lube oils (safflower contaminant) will confirm the results of Figure 1

and extend the technology to commercial lube oil systems containing stabilizing additives. The projected economics of ZDTC as a further additive look promising. Its cost in bulk is \$1.30/lb (as 50% active in mineral oil), a figure that would increase the price of a gallon of lube oil less than \$0.10. In addition, this additive could possible substitute for an existing antioxidant (maybe ZDTP), resulting in no higher lube oil cost.

Insoluble Gel Characterization

The nature of insoluble gel and its relation to viscosity build-up must be understood before it can be minimized and before additive-free basestocks can be used for further work. Several experiments were conducted to determine whether this gel is merely an insoluble linear polymer or a more complex, perhaps crosslinked, chemical species.

Insoluble gel from an SAE 30 basestock trial was decanted from supernatant and then mixed at 5.0% in SAE 30 commercial lube oil. The mixture was heated with agitation to 150°C and held for 10 hours. Throughout the test the mixture was examined for evidence of gel dissolution. There was no discernible loss of solid gel, although there was a definite softening. This result seems to show that the gel

is not the same chemical species that causes viscosity rise in the commercial oil. It was surmised that the materials might be the same and that lack of a dispersant in basestock oil leads to a precipitated solid polymer form.

Gel swollen with basestock oil was next subjected to high speed comminution in a laboratory blender in an attempt to form a thickened homogeneous liquid phase. Blending at intervals up to 105 minutes failed to produce homogeneity. This second failure to produce a true solution or even a colloidal dispersion by physical means again indicates that gel may not be the same material that causes viscosity rise in commercial SAE 30 experiments.

Finally, a widely used industrial oil dispersant Paronox 107 (succinimide-based) was tested in an attempt to disperse gel in basestock oil at 150°C. No apparent loss of solid phase was noted throughout this extended test at 150°C. Once again a thickened liquid phase was not achieved.

The general conclusion of the three experiments cited above is that the insoluble gel formed in sunflower/basestock experiments is fundamentally different from the soluble polymer that produces viscosity build-up in sunflower/commercial lube trials. The gel polymer may be

insoluble due to crosslinking or to a certain molecular weight distribution that differs from that formed in the commercial lube oil trials. Presumably, the additives in commercial lube oil play a role, but an unknown one at present. In any case, either viscosity rise or gel formation pose a major obstacle to the use of plant oil fuels.

Catalysis

Since the beginning of this study, the significant role of copper as a polymerization catalyst has been known. As reported in Milestones #1 through #3 copper, especially dissolved species, accelerates polymerization while having little impact on alkalinity. Along with copper, iron was investigated as a catalyst early in this study. By itself or combined with copper, iron showed no catalytic effect on polymerization in repeated trials. Other engine wear metals, in particular lead, aluminum and silver, were recently studied for catalytic impact.

Lead, aluminum and silver were tested separately as catalyst foils in standard 150°C exposures of 5.0% sunflower oil in SAE 30 commercial lube oil. No catalytic behavior was found for any of these metals. Viscosity curves for each metal tested matched the "no copper" standard case

within experimental precision. At 24 hours samples were taken from each trial cell and tested by atomic emission spectroscopy for dissolved metals. Duplicate testing showed no dissolved lead or silver and only trace aluminum in their respective trials. These metals may be catalytically active as dissolved species, but little or none of such materials were detected in this phase of the work. This item may be a topic for future research.

Work is continuing to identify chemical agents that deactivate catalysis of dissolved copper species. Several commercially available agents purported to deactivate metals in general oxidation reactions were tested with no impact on oil mixture viscosity. However, a promising new candidate has been found which has a major impact on polymerization rate with copper in the laboratory apparatus. The compound is N, N' disalicylidine-1,2 propane diamine (NNPD) from Dupont. Figure 2 shows the impact of NNPD on viscosity rate of rise at three addition levels (75% active NNPD in xylenes). The dashed line is the standard case - copper foil, 5.0% sunflower, 150°C, O₂ flow - with no NNPD. Obviously the additive retards polymerization, but whether metal deactivation is the mechanism is as yet uncertain. Further research will seek to clarify the mechanism of NNPD's efficacy.

Specialty compounds such as NNPD are not yet produced in bulk by Dupont, but a projected commercial selling price is \$4.14/lb. At this price, the compound (or others like it) must be effective at less than one percent to control oil cost at reasonable levels. Again, the additives may substitute for another costly deactivator already present in a commercial "package", thus minimizing added cost.

Clearly, additives that show benefits separately such as ZDTC and NNPD may yield synergism when combined. However, the individual mechanisms are not understood at this point, and any combined effects would be even less understood. Thus, continued research will deal with the individual additives until a point is reached at which meaningful conclusions can be drawn from their combination.

Other Milestone Highlights

Research on the problems posed for a diesel engine lubrication system by plant oil fuel will continue under DNRC grant RAE-86-1067. The focus will be Montana-specific safflower oil contamination in medium speed diesel lubrication oil.

A draft of the final report for grant RAE-84-1040 will be submitted to DNRC by August 1, 1986.



